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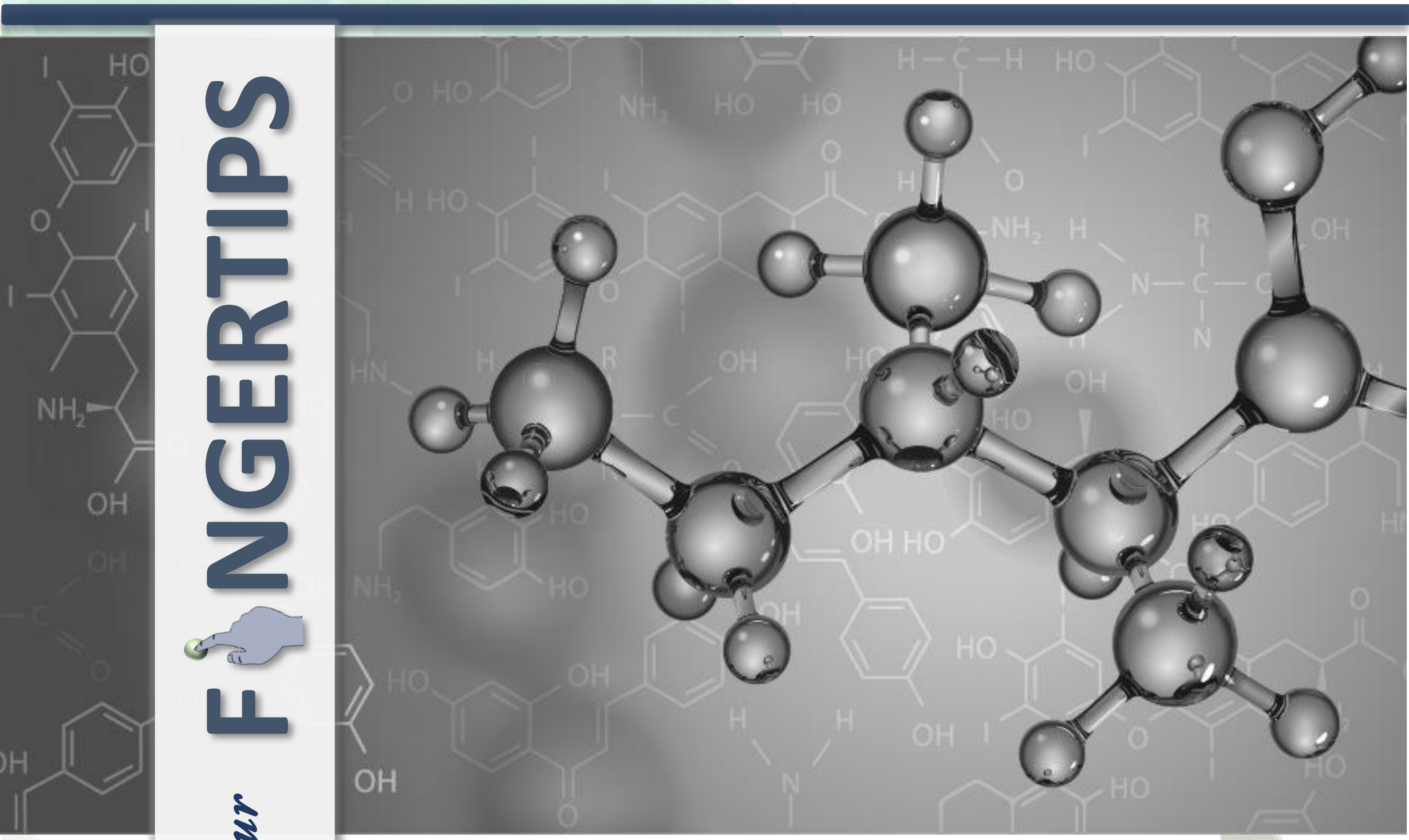

2024

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CHEMISTRY

MODULE – 7

Hornbill
classes

EDITION : 2024

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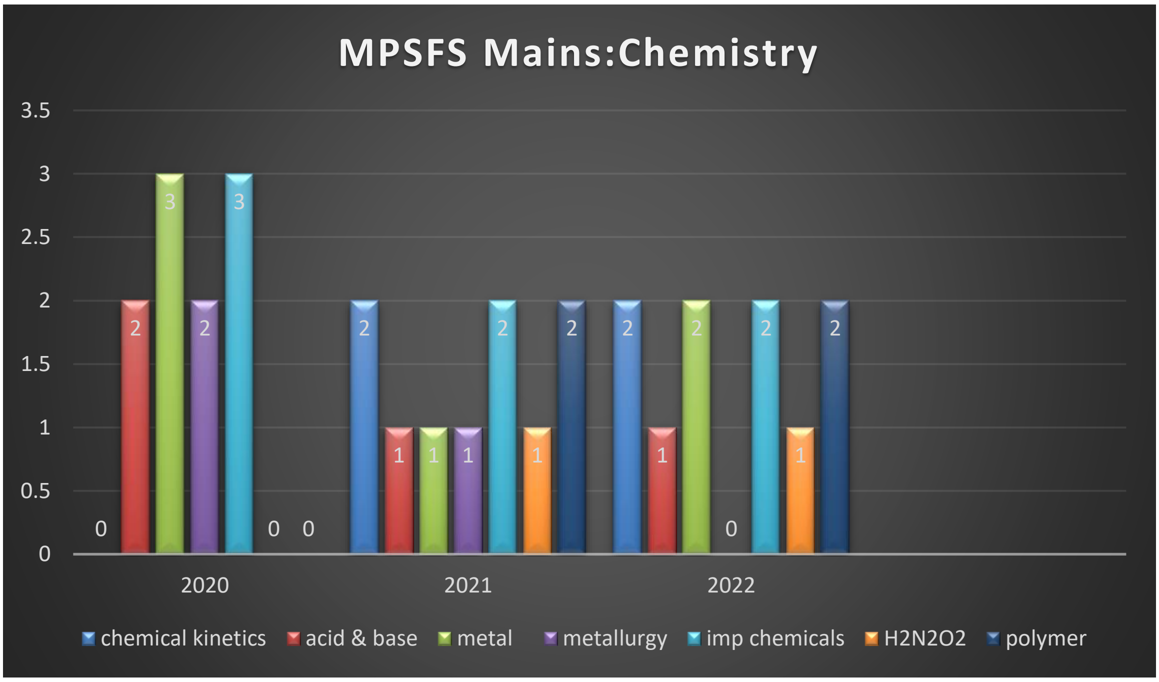
SYLLABUS

Unit	Syllabus
1	**CHEMICAL EQUILIBRIUM**: Definition, types of Equilibrium, Factors Affecting Equilibrium, Le-Chatelier's Principle. **LAW OF MASS ACTION**: Introduction, Equilibrium Constant, Equilibrium Constant in Gaseous System, Factors Affecting Equilibrium Constant. **LE-CHATELIER'S PRINCIPLE**: Definition
2	**CHEMICAL KINETICS**: Introduction, Rate of reaction, factors affecting rate of reaction, rate law, average rate of reaction, units of rate constant, order of reaction, half live period of reactions. **DIFFERENT TYPES OF REACTION:** reversible and irreversible reaction, endothermic & exothermic reaction, fast & slow reactions
3	**ACIDS & BASES**: Introduction, properties and uses of acids & bases, different concepts of acids & bases (Arrhenius, Bronsted-Lowry, Lewis), conjugate acids & bases, HSAB concept. **pH SCALE**: pH discovery, pH of acids, bases & water, dissociation constant, some examples.
4	**CHEMICAL COMPOUND**: water: properties and uses, hard & soft water, heavy water. **PREPARATION, PROPERTIES & USES OF**: washing soda, baking soda, bleaching powder, plaster of Paris, gypsum. **PREPARATION OF BUILDING MATERIALS**: lime, cement, glass, steel
5	**METALS & THEIR PROPERTIES**: Introduction, position of metals in periodic table. **NON-METALS**: Introduction, position of non-metals in periodic table. **ORES & ALLOYS**: Types and examples.
6	**METALLURGY**: Introduction, steps involved in the extraction of metals: concentration (gravity separation, magnetic separation, froth flotation), conversion of ores into oxide (calcination, roasting), reduction of ore (different processes). **METALLURGY OF COPPER & IRON**: Introduction & process **CORROSION OF METALS**: Introduction, electrochemical theory of rusting, factors affecting corrosion.

7	**HYDROGEN**: preparation, isotopes, types, properties and uses. **OXYGEN**: preparation, properties and uses. **NITROGEN**: preparation, properties and uses. **ALCOHOL**: preparation, types, properties and uses. **ACETIC ACID**: preparation, properties and uses.
8	POLYMER: introduction, types rubber, nylon, polythene, Teflon, PVC, Bakelite, biodegradable polymer, resin soaps & detergents.



INDEX

CHEMISTRY

CHAPTER
1

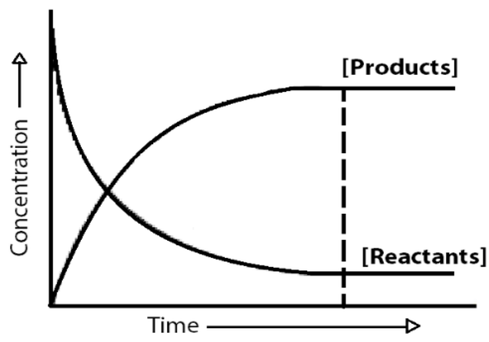
CHEMICAL EQUILIBRIUM

Syllabus: Chemical Equilibrium, Types of Equilibrium, Factors Affecting Equilibrium, Law of Mass Action and Equilibrium Constant, Equilibrium Constant in Gaseous System, Factors Affecting Equilibrium Constant, Le-Chatelier's Principle.

1.1 INTRODUCTION

The state of any reversible process(reaction) in which rate of the forward and the backwards (reverse) reactions are equal is called chemical equilibrium. In this state, the measurable properties of the system like concentration, temperature, colour, density etc. Don't undergo any change with time and remain constant.

Attainment of Chemical Equilibrium



$a + b \leftrightharpoons c+d$
Now, a + b = forward reaction
c + d = backward reaction
Then, according to law of mass action:
rate of forward reaction (r_f) α [a] [b]
$(r_f) = k_f\,[a]\,[b]$ (k_f = constant)
and rate of backward reaction (r_b) α [c] [d]
$(r_b) = k_b\,[c]\,[d]$
Now, equilibrium = $(r_f) = (r_b)$
$k_f[a]\,[b] = k_b\,[c]\,[d]$
$\frac{K_f}{K_b} = \frac{[C]\,[D]}{[A]\,[B]} = k_c$

Here k_c is known as the Equilibrium Constant and has a definite value for every chemical reaction at a particular temperature.

Note: This equilibrium is dynamic in nature as it consists of a forward reaction in which reactants give products and backward rection in which product gives original reactants. Even after equilibrium, the reactants & products are changing into each other and this equilibrium state can be approached from both sides.

Ex: synthesis of ammonia by Haber's process.

$N_2 + 3h_2 \leftrightharpoons 2nh_3$

This reaction also indicates that chemical reaction reaches a state of dynamic equilibrium, in which the rates of forward & backward reactions are equal and there is no net change in composition.

1.2 TYPES OF EQUILIBRIUM

- **Homogenous equilibrium:**

  A system where all the reactants and products are in same phase.

  Ex: $N_2\,(g) + 3H_2\,(g) \leftrightharpoons 2\,NH_3\,(g)$

- **Heterogeneous equilibrium:**

  Equilibrium in a system having more than one phase is called heterogenous equilibrium.

  For ex:

  The equilibrium between water vapour & liquid water in a closed container is heterogeneous equilibrium

  $H_2O(l) \leftrightharpoons H_2O(g)$

  (liquid phase)   (gas phase)

  Heterogeneous equilibrium often involves pure solids or liquids and the molar concentration of pure solid/ liquid is constant.

  Ex: $CaCO_3\,(s) \leftrightharpoons CaO(s) + CO_2(g)$

  In this reaction the constant concentration of CO_2 is in equilibrium with CaO(s) & $CaCO_3$(s).

1.3 FACTORS AFFECTING EQUILIBRIUM

Equilibrium of any system is affected temperature, volume, pressure, concentration of reactant/product.

(i) **Temperature:**

- The equilibrium constant for an exothermic reaction decreases as the temperature increases.

  $k_{exo} \propto 1/T$

- The equilibrium constant for an endothermic reaction increases as temperature increases. $k_{endo} \propto t$

There is an absorption of energy as the temperature increases and emission of energy as the temperature decreases.

(ii) **Pressure**

There is a very low effect of pressure change in solids & liquids and can be ignored because the concentration (volume) of solids /liquids is nearly independent of pressure. But in gaseous reaction pressure change is obtained by changing the volume and it eventually affect the yield of the product.

If $\delta ng = 0$, pressure has no effect

If $\delta ng > 0$, the equilibrium will get shifted to backward direction on increasing pressure

If $\delta ng < 0$, the equilibrium will shift towards forward direction on increasing pressure

(iii) **Concentration**

At equilibrium concentration of products increases by increasing in concentration of reactants and vice-versa.

(iv) **Catalyst**

It does not affect equilibrium.

(v) **Inert gas**

If an inert gas is added (which does not take part) in the reaction, the equilibrium remains unchanged.

1.4 LAW OF MASS ACTION

This law was given in 1864 by Guldberg & Wage, they stated that 'at given temperature the rate of any chemical reaction is directly proportional to the product of the active masses (concentration) of the reactants.'

let's take an equation

a + b ⇋ c + d

for this

Equilibrium Constant $k_c = \frac{[C]\,[D]}{[A]\,[B]}$

Here the expression on the right side is called equilibrium constant expression.

The equilibrium constant for a general reaction:

aA + bB ⇋ cC +dD [forward reaction]

Is expressed as

$k_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$

This means reaction products are in numerator & reactants are in denominator. In a balanced equation, each concentration is expressed as power of their stoichiometric coefficient.

Note: Always take the concentration of solid as 1 & in liquid only water has a concentration as 1,

[solid] = 1, $[H_2O] = 1$

For ex:

(i) $4NH_3 + 5O_2$ ⇋ $4NO + 6H_2O$

So, equilibrium constant $k_c = \frac{[NO]^4[H_2O]}{[NH_3][O_2]^5}$

(ii) $CaCO_3$ (s) ⇋ CaO (s) + CO_2 (g)

Here $k_c = [CO_2]$ (because active mass of solid is 1)

Similarly for reverse reaction:

Let's take an equation $H_2 + I_2$ ⇋ 2HI

Now, equilibrium cons. $K_c = \frac{[HI]^2}{[H_2][I_2]} = x$ (let)

Now equilibrium constant for reverse reaction

2hi ⇋ $h_2 + i_2$, at the same temperature

is $k'c = \frac{[[H_2][I_2]}{[HI]^2} = \frac{1}{x}$

Or, $k'c = \frac{1}{x} = \frac{1}{K_c}$

Chemical Equation	Equilibrium Constant
aA + bB ⇋ cC +dD	K_c
cC +dD ⇋ aA + bB	$K_c' = 1/k_c$

So, equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction of forward direction.

EQUILIBRIUM CONSTANT IN GASEOUS SYSTEM

Here we express the equilibrium constant in terms of partial pressure

for a general equation –

a + b ⇋ c + d

$k_p = \frac{P_C \times P_D}{P_{A\times}\,P_B}$

- **Relation b/w k_p and k_c:**

$K_p = \frac{P_C}{P_A}\frac{.P_D}{.P_B} = \frac{[C]^c}{[A]^a}\frac{[D]^d}{[B]^b}\frac{RT^{(c+d)}}{RT^{(a+b)}}$ $\left\{P = \frac{n}{V}RT = CRT\right\}$

$= \frac{[C][D]}{[A][B]}(RT)^{(c+d)-(a+b)}$

$= \frac{[C][D]}{[A][B]}(rt)^{\Delta n} = k_c(rt)^{\Delta n}$

or, $k_p = k_c (rt)^{\Delta n}$

Where Δn = number of gaseous atoms in product - number of gaseous atoms in reactant.

Note: (only gaseous moles are taken in this, not solids or liquids.)

When $\Delta n_g = 0$, then $k_p = k_c$

When $\Delta n_g < 0$, then $k_p < k_c$

When $\Delta n_g > 0$, then $k_p > k_c$

For ex:

(i) $H_2(g) + I_2(g) \leftrightharpoons 2Hi(g)$

$\Delta n_g = 2 - (1+1)$ [no. Of product – no. Of reactant]

2-2=0

$\Delta n_g = 0$

$k_p = k_c$

(ii) $N_2(g) + 3H_2O \leftrightharpoons 2NH_3(g)$

Now, $\Delta n = 2-(3+1)$

= 2-4

$\Delta n_g = -2$, $\Delta n_g < 0$

Now putting the value of Δn:

$K_p = k_c (rt)^{\Delta n}$

$K_p = k_c (rt)^{-2} = \frac{k_c}{(RT)^2}$

$K_p = \frac{k_c}{(RT)^2}$, $k_p < k_c$

(iii) $PCL_5 \leftrightharpoons PCL_3 + Cl_2$

now, $\Delta n_g = 1+1-(1)$

=2-1

$\Delta n_g = 1$, $\Delta n > 1$

$k_p > k_c$

Unit of k_p and k_c:

Unit of $k_p = (atm)^{\delta n}$

Unit of $k_c = (mol.\ L^{-1})^{\delta n}$

If $\delta n_g = 0$, no unit of k_p & k_c

LE-CHATELIER'S PRINCIPLE

It is also known as equilibrium law. It states that, "if a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium shifts to counteract the change to re-established an equilibrium."

Means if a chemical reaction is at equilibrium, experiences a change in pressure, temperature or concentration of reactants/products, the equilibrium shifts in the opposite direction to off-set the change.

Que. निम्नलिखित साम्यों में किसके लिए K_c एवं K_p का मान समान होगा: [CGACF 2016]

(a) $PCL_5 \rightleftarrows PCl_3 + Cl_2$

(b) $2SO_2 + O_2 \rightleftarrows 2SO_3$

(c) $H_2 + I_2 \rightleftarrows 2HI$

(d) $N_2 + 3H_2 \rightleftarrows 2NH_3$

(e) ईनमें से कोई नहीं

Here answer will be option (c). as mentioned above in ex 1 the value of K_p & K_c will be same for option (c).

FACTORS AFFECTING EQUILIBRIUM CONSTANT(K)

Only 2 factors affect the equilibrium constant

(i) Temperature: for exo = $k_{exo} \propto \frac{1}{T}$, for endo. = $k_{endo} \propto t$

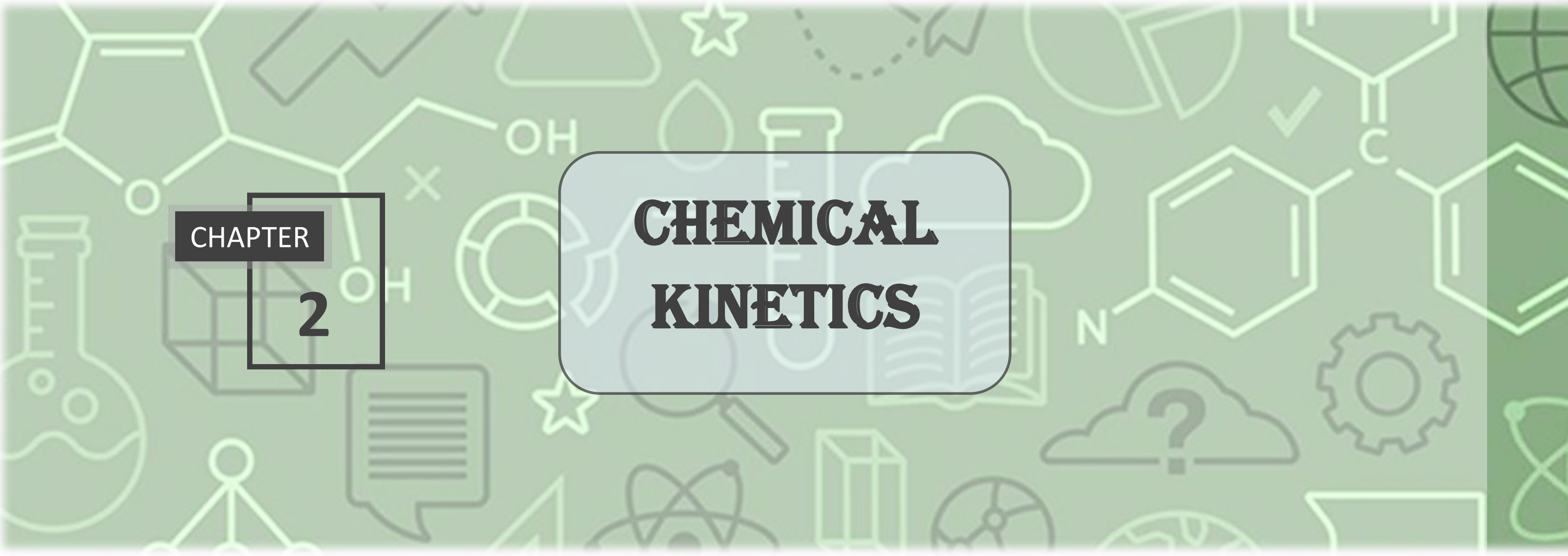
(ii) Direction of reaction

Apart from these 2, no other factor affects the equilibrium constant(k).

Exercise no 1

1. In decomposition reaction of ammonia $2NH_{3(g)} \rightleftharpoons N_2(g) + 3H_2(g)$
   2 moles of NH_3 are introduced in the vessel of 1 litre. At equilibrium 1 mole of NH_3 was left, the value of equilibrium constant (K_c) will be [CG pariyojna 2021]
   (a) 0.688
   (b) 1.688
   (c) 0.0688
   (d) 1.788
2. $A + 2B \leftrightharpoons 2C + D$
   1 mole of A reacts with 1.5 mole of B in such a way that at equilibrium number of moles of A and D are equal. The equilibrium constant will be [CG Vyapam RFO 2021]
   (a) 1.0
   (b) 2.5
   (c) 3.2
   (d) 4.00
3. Which statements is not correct? [MPPSC SFS Main 2021]
   (a) Chemical equilibrium is a dynamic equilibrium
   (b) Properties measured at equilibrium remain constant
   (c) Presence of catalyst affects chemical equilibrium
   (d) Catalyst only establishes chemical equilibrium rapidly

(1.) b, (2.) d, (3.) d



CHAPTER 2

CHEMICAL KINETICS

Syllabus: Rate of reaction, factors affecting rate of reaction, rate law, average rate of reaction, units of rate constant, order of reaction, half live period of reactions, reversible and irreversible reaction, endothermic & exothermic reaction, fast & slow reactions

2.1 INTRODUCTION

- Chemical kinetics = Kinesis (Greek word) = movement
- The **Rate of reaction** can be defined as the change in concentration of a reactant or product per mol in unit time. This means it is the speed at which reactants are converted into products:
  (i) The rate of decrease in concentration of any reactant.
  (ii) The rate of increase in concentration of any product.

Let’s take a general equation at constant volume:

$$R \rightarrow P$$

At time t_1 = concentrations of R & P are $[R]_1$&$[P]_1$

And, at time t_2 = concentrations of R & P are $[R]_2$& $[P]_2$

Then rate of disappearance of R

= (Decrease in concentration of R)/ (Time)

= $-\Delta[R]/\Delta t$ ----------------- (i)

And rate of appearance of P

= (Increase in concentration of P)/ (Time)

= $+\ \Delta[P]/\Delta t$-----------------(ii)

Here $\Delta[R]$ is taken negative because concentration of reactants is decreasing and $\Delta[P]$ is taken positive because concentration of products is increasing with time.

Units of rate of reaction: according to equation (i) & (ii) the units of rate are

= concentration x time^{-1}

For example, if concentration is in mol/l and time is in seconds then the units will be

= mol. L^{-1}. s^{-1}

Note: for expressing the rate of any reactions where stoichiometric coefficient of reactant/product are not equal to one, then rate of disappearance or appearance is divided by their stoichiometric coefficient.

For ex:

2HI → H2 + I2

Rate of reaction = $-\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$

2.2 FACTOR AFFECTING RATE OF REACTION

(i) Concentration: the more concentrated the reactants, the faster the rate will be.

(ii) Temperature: generally, reactions speed up with increasing temperature.

(iii) Physical state of reactants: powders react faster than blocks.

(iv) Presence of a catalyst: a catalyst speeds up a reaction, an inhibitor slows it down.

(v) Light: light of a particular wavelength may also speed up a reaction.

(vi) Pressure: in gases the number of collisions increases with increase in partial pressure, resulting increase in the rate of reactions.

Exercise no 1

1. Which of the following **does not** affect the rate of a reaction? [CGPSC ACF 2020]
   (a) Concentration of reactant molecules
   (b) Number of molecules taking part in the reaction
   (c) Nature of reactant molecules
   (d) Temperature

(1.) b

2.3 RATE LAW

The actual relationship between the concentration of reacting species and the reaction rate is determined experimentally and is given by the expression called rate law.

For any reaction:

$$aA + bB \rightarrow cC + dD$$

Rate law expression may be, rate = $k[A]^x [B]^y$

Where x and y are powers of the concentrations of the reactants A & B.

(i) Rate of chemical reaction is directly proportional to the concentration of the reactants.

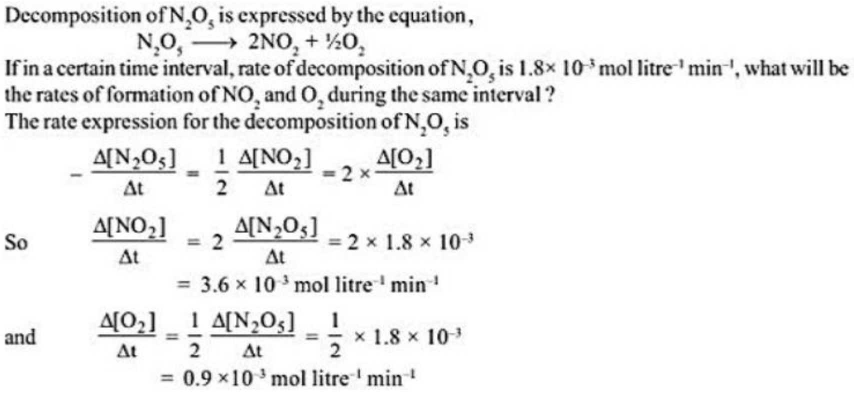
(ii) Rate law cannot be deduced from the relationship for a given equation. It can be found by experiment only.

2.4 CALCULATION OF AVERAGE RATE OF REACTION:

To calculate the average rate of reaction between any two instants of time say t_1 and t_2, the corresponding concentrations x_1 and x_2 are noted from the graph. Then,

Average rate of reaction = $\frac{X2 - X1}{T2 - T1}$

for example:



Decomposition of N_2O_5 is expressed by the equation,

$$N_2O_5 \longrightarrow 2NO_2 + ½O_2$$

If in a certain time interval, rate of decomposition of N_2O_5 is 1.8×10^{-3} mol litre^{-1} min^{-1}, what will be the rates of formation of NO_2 and O_2 during the same interval ?

The rate expression for the decomposition of N_2O_5 is

$$-\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2}\frac{\Delta[NO_2]}{\Delta t} = 2 \times \frac{\Delta[O_2]}{\Delta t}$$

So $$\frac{\Delta[NO_2]}{\Delta t} = 2\frac{\Delta[N_2O_5]}{\Delta t} = 2 \times 1.8 \times 10^{-3}$$
$$= 3.6 \times 10^{-3} \text{ mol litre}^{-1} \text{ min}^{-1}$$

and $$\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2} \times 1.8 \times 10^{-3}$$
$$= 0.9 \times 10^{-3} \text{ mol litre}^{-1} \text{ min}^{-1}$$

2.5 ORDER OF REACTION

The order of a reaction refers to a relationship between the rate of a reaction and the concentration of the species taking part in it. “In the rate law expression, the sum of powers of the concentration of reactants is called the order of that chemical reactions.”

- The order of reaction does not depend on the stoichiometric coefficient corresponding to each species in the balanced reaction.
- The order of reaction is always defined with the help of **reactant concentration** and not with product concentration.
- The value of the order of reaction can be zero, a fraction or an integer.

For ex: calculate the overall order of reaction which has the rate expression –

(a) $K[A]^{1/2}[B]^{3/2}$
(b) $K[A]^{3/2}[B]^{-1}$

Solve:

(a) Rate = $k[A]^x[B]^y$ {from rate equation}

Now order = $x + y = \frac{1}{2} + \frac{3}{2} = \frac{4}{2} = 2$

= second order

(b) Order = $x + y = \frac{3}{2} - 1 = \frac{1}{2}$

= half order

2.6 UNITS OF RATE CONSTANT

For a general reaction – $aA + bB \rightarrow cC + dD$

rate = $k[A]^x[B]^y$ ---------- (i)

where order of reaction = x + y = n

now, $k = \frac{Rate}{[A]^x[B]^y}$ { from eq. ------ (i) }

$= \frac{Concentration}{Time} \times \frac{1}{(conc.)^n}$

= $(concentration)^{1-n}. Time^{-1}$

Table: units of rate constant

Reactions	Order	Units of rate constant
Zero order reaction	0	$\frac{Mol.L^{-1}}{s} \times \frac{1}{(Mol.L^{-1})^0}$ = $mol.\ l^{-1}.\ S^{-1}$
First order reaction	1	$\frac{Mol.L^{-1}}{s} \times \frac{1}{(Mol.L^{-1})^1}$ = s^{-1}
Second order reaction	2	$\frac{Mol.L^{-1}}{s} \times \frac{1}{(Mol.L^{-1})^2}$ = $mol^{-1}.\ L.\ S^{-1}$
Nth order reaction	N	$\frac{Mol.L^{-1}}{s} \times \frac{1}{(Mol.L^{-1})^n}$ = $mol^{1-n}.\ L^{n-1}.\ S^{-1}$

For ex: $H_2(g) + I_2(g) \leftrightharpoons 2HI(g)$, order of reaction =? [when r = k]

Solve: now $r = k[h_2]^0 [i_2]^0$ [$x^0 = 1$]

So, the order of reaction will be:

0+0=0 zero order

For zero order reaction:

Rate of reaction(r) = rate constant (k)

- **Trick to get unit of k:**

  $k= (mol.\ L^{-1})^{1-n}.\ s^{-1}$

  Ex (1): 3rd order reaction:

  $K = (mol.\ L^{-1})^{1-3}.\ S^{-1} = (mol.\ L^{-1})^{-2}.\ S^{-1}$

  $K = mol^{-2}\ l^2.S^{-1}$

Ex (2): if $k= 3\times10^{-3}\ mol^{-2}.\ L^2.s^{-1}$, find the order of the reaction?

Solve: as we know unit of $k = (mol.\ L^{-1})^{1-n}.\ S^{-1}$

or $k = (mol/l)^{1-n}.\ S^{-1}$

now comparing the units:

$\left(\frac{mol}{l}\right)^{1-n} .\ S^{-1} = \left(\frac{mol}{l}\right)^{-2} .\ S^{-1}$

1-n = -2

n = 3, means it is a third order reaction.

Ex (3): 2a + 3b → product, if order of reaction with respect to a is 2 and order of reaction with respect to b is -1, then calculate the order of reaction and write rate law equation? What is the effect on rate when (a) concentration of a is doubled alone? (b) concentration of b is halved alone?

Solve: rate of reaction(r) = $k\ [A]^2[B]^{-1}$

order of reaction = 2+(-1) =1, first order reaction.

(a) Initial concentration $r= k[A]^2[B]^{-1}$

When doubled $r'= k[2A]^2[B]^{-1}$

Now dividing these:

$\frac{r'}{r} = K[2A]^2[B]^{-1} / k[A]^2[B]^{-1}$

$\frac{r'}{r} = 4$

or, r' = 4r, that means rate increases 4 times.

(b) Initial concentration $r= k[A]^2[B]^{-1}$

When halved $r'= k[A]^2[B/2]^{-1}$

Now, $\frac{r'}{r} = k[A]^2[B/2]^{-1} / k[A]^2[B]^{-1}$

$\frac{r'}{r} = 2$

or r'= 2r, that means rate increases 2 times.

2.7 HALF - TIME OR HALF - LIFE PERIOD:

For zero order reaction:

At $t = t_{1/2}$ and $x= a/2$,

$t_{1/2} = \frac{a}{2k}$ or $t_{1/2} \propto a$

For first order reaction:

The half - time of a reaction is defined as the time required to reduce the concentration of the reactant to half of its initial value. It is denoted by the symbol $t_{1/2}$. Thus, **for first order reaction**:

K= $\frac{2.303}{t}\log\frac{a}{a-x}$ where k= rate constant, t= time

Similarly for time t= $\frac{2.303}{k}\log\frac{a}{a-x}$

When x = a/2, t = $t_{1/2}$, now putting these values in above equation:

K = $\frac{2.303}{t_{1/2}}\log\frac{a}{a-\frac{a}{2}}$

k = $\frac{2.303}{t_{1/2}}\log_e 2$

Or, $t_{1/2} = \frac{0.693}{k}$ [$\log_e 2 = 0.693$]

For nth order reaction:

for nth order reaction, the half-life is inversely related to the initial concentration raised to the power of (n – 1):

$t_{1/2} \propto \frac{1}{a^{n-1}}$

1. For the first order reaction, the time required for 99.9% completion of reaction is how many times that required for 50% completion? [Raj ACF 2018]

(a) 50 times

(b) 10 times

(c) 5 times

(d) 2.5 times

Solve- t= $\frac{2.303}{k}\log\frac{a}{a-x}$

$T_{99.9} = \frac{2.303}{k}\log\frac{100}{100-99.9} = = \frac{2.303}{k}\log\frac{100}{1}$

$= \frac{2.303}{k}\log_{10}1000$---------**(i)**

Now, $T_{50} = \frac{2.303}{k}\log\frac{100}{100-50} = \frac{2.303}{k}\log_{10}2$------**(ii)**

Now dividing both the equation: $= \frac{3.000}{0.3010} = 10$

2. The $t_{1/2}$ of reaction is doubled as the initial concentration of the reactant is doubled. What is the order of the reaction? [Raj ACF 2018]

(a) 3

(b) 2

(c) 1

(d) 0

Solve: we know that half -life is related to concentration as

$t_{1/2} \propto \frac{1}{a^{n-1}}$

according to question,

$\frac{t_{1/2}}{2t_{1/2}} = \frac{1/a^{n-1}}{1/2a^{n-1}}$

$½ = 2^{n-1}$

$2^{-1} = 2^{n-1}$

n-1 = -1

n=0, hence the reaction is of the zero order.

3. A first order reaction A → product has a first order rate constant $1.15 \times 10^{-3}s^{-1}$ how long it will take 8.0 g of A to reduce to 2.0 g? [Raj ACF 2018]

(a) 802 s

(b) 1205 s

(c) 601 s

(d) 200 s

Solve: t= $\frac{2.303}{k}\log\frac{R_0}{R}$

$= \frac{2.303}{1.15\times10^{-3}}\log\frac{8}{2}$

$= 2.00 \times 10^3 \log 4$

= 2000 × 0.60206

t = 1205 s

4. The reaction A → product is zero order while reaction B→ product is first order reaction. for what initial concentration of A, the half-lives of two reactions are equal? [CG pariyojna 2021]

(a) Log_e4M

(b) $\frac{1}{2} log_e2M$

(c) log_e2M

(d) $4\ log_e2M$

Solve: for a zero-order reaction, concentration at any time

$t_{1/2} = \frac{a}{2k}$-------**(i)**

for a first order reaction,

$t_{1/2} = \frac{log_e2}{k}$------**(ii)**

from (i) and (ii)

$\frac{a}{2k} = \frac{log_e2}{k}$

Or, a = log_e4 M

Answer Key
1. (b), 2. (d), 3. (b), 4. (a)

2.8 REVERSIBLE AND IRREVERSIBLE REACTIONS

- **Irreversible reactions:** the reactions which can occur in only one direction is called an irreversible reaction. In this the reaction can change back to the products. But the products cannot change back to the reactants. For example:

1. **Nutalization Reaction**: A reaction where an acid & a base react together to form a salt & water.

   Acid + Base → Salt + Water

   $HCl + NaOH \rightarrow NaCl + H_2O$

2. **Precipitation Reaction:** A reaction where two different soluble salts in aqueous solution combine to form a precipitate that is insoluble in solution.

   Ex: $AgNO_3 + KCl \rightarrow \underset{\text{(precipitate)}}{AgCl} + KNO_3$

3. **Combustion Reaction:** A reaction where a substance reacts with O_2 gas, releasing energy in the form of light & heat.

   Ex: $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ = (water vapour)

4. **Thermal Decomposition:**

   A reaction where a compound breaks down or decompose when heated and give a variety of products.

   ex: $ZnCO_3(s) \xrightarrow{Heat} ZnO\ (s) + CO_2 \uparrow$

   Note: The thermal decomposition of $CaCO_3$ is reversible reaction in closed pot and irreversible reaction in open pot as well.

5. **Redox Reaction:**

   Reactions that involve the transfer of electrons from one species to another. The one loses electrons is said to be oxidized, while the one gains electrons is said to be reduced.

   It consists of 2 reactions:

(a) **Oxidation:** addition of O_2/removal of H_2

ex: $2S(s) + O_2(g) \rightarrow 2SO_2(g)$

(b) **Reduction: -** Removal of o_2/ gain of h_2

ex: $2FeCl_3(aq) + H_2(g) \rightarrow 2Fecl_2\ (aq) + 2HCl(aq)$

- **Reversible reaction:** the reaction which occurs in both direction is called reversible reaction. In this the reactants and the products are converted to each other. These reactions are bidirectional and happens in a closed system. These reactions are sometimes very slow and may proceeds till infinity. An equilibrium condition also occurs in this. gibs free energy of these are taken as zero.

  Ex: $N_2(g) + 3H_2(g) \leftrightarrows 2NH_3(g)$

  Types: (i) homogeneous: whole reaction is in same phase.

  Ex: $N_2(g) + 3H_2(g) \leftrightarrows 2NH_3(g)$

  (ii) heterogeneous: reaction occurs in different phases.

  ex: $CaCO_3(s) \leftrightarrows CaO(s) + CO_2\ (g)$

  Details are given back in equilibrium chapter.

  Note: if the reaction is isothermal then temperature is constant, if the reaction is isobaric then pressure is constant and if the process is isochoric then volume is constant.

Exercise no 3

1. Neutralization reaction: [MPPSC SFM 2018]
   $KOH_{(aq)} + HCl_{(aq)} \rightarrow KCl_{(aq)} + H2O$---- is an example of which the following type of reaction:
   (a) Reversible reaction
   (b) Irreversible reaction
   (c) Both reversible and irreversible reaction
   (d) None of these
2. In a reversible isothermal process? [MPPSC SFM SP 2019]
   (a) P is constant
   (b) T is constant
   (c) Both P and T are constant
   (d) Neither P nor T are constant
3. (A) $AB + C \rightarrow CB + A$ [MPPSC SFS Main 2021]
   (B) $AB+C \rightleftharpoons CB + A$
   Which statement is correct for reactions (A) and (B)?
   (a) (A) Reversible and (B) Irreversible
   (b) (A) Irreversible and (B) Reversible
   (c) (A) and (B) both are Reversible
   (d) (A) And (B) both are Irreversible
4. Which statement is false? [CGPSC ACF 2020]
   (a) The grater the concentration of the substance involved in a reaction, the lower the speed of the reaction
   (b) The point of dynamic equilibrium is reached, when the reaction rate in one direction just balances the reaction rate in the opposite direction
   (c) The dissociation of weak electrolyte is a reversible reaction
   (d) The presence of free ions facilities chemical changes
5. An example of reversible reaction is [CGPSC ACF 2017]
   (a) $AgNO_{3(aq)} + HCl_{(aq)} \rightarrow AgCl_{(s)} + HNO_{3(aq)}$
   (b) $2Na + 2H_2O \rightarrow 2NaOH + H_2 \uparrow$
   (c) $NaOH + CH_3COOH \rightarrow CH_3COONa + H_2O$
   (d) $Pb(NO_3)_2 + 2NaI \rightarrow PbI_2 + 2NaNO_3$
   (e) None of these
6. The thermal decomposition of $CaCO_3$ is [CGPSC ACF 2017]
   $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$
   (a) It is reversible reaction in closed pot
   (b) It is irreversible in open pot
   (c) Both a and b are correct
   (d) Reaction equation Is wrong
   (e) None of these
7. The combination of $H^+ + OH^- \rightarrow H_2O$ is called [CGPSC ACF 2017]
   (a) Hydrolysis
   (b) Neutralisation
   (c) Dehydration
   (d) Dehydrohalogenation
   (e) None of these

(1.) b, (2.) b, (3.) b, (4.) a, (5.) c, (6.) c, (7.) b

2.9 ENDOTHERMIC & EXOTHERMIC REACTIONS

- **Endothermic reaction:** a reaction where the system absorbs the energy from its surrounding in the form of heat, is called endothermic reaction. It occurs as result of dissociation of the bonds between the molecules. The energy is then released through the formation of new bonds. Since heat is taken up from the surroundings in this reaction so the temperature of the system remains cooler. Also, the enthalpy (change in heat energy during reaction) increases at the end of the reaction.

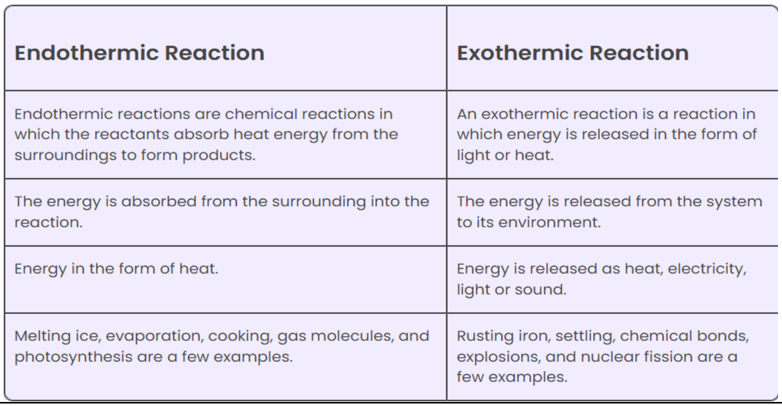
Ex: photosynthesis, evaporating liquid, melting ice, dry ice, alkane cracking, thermal decomposition, fusion, sublimation, formation of quick lime from limestone etc.

- **Exothermic reaction:** a reaction where the system releases energy in the form of light & heat to its surrounding, is called exothermic reaction. During chemical reactions, a great deal energy is required and as result of reaction and breaking of bonds as well, an enormous amount of energy is released. At the end of the reactions, the enthalpy decreases as well.

  Ex- neutralization, burning a substance reaction of fuels, respiration, condensation, deposition, dissolving of acids, and anhydrous sodium carbonate in water.

Exercise no 4

1. The nature of the reaction of formation of quick lime from limestone is [MPPSC SFS Main 2019]
   (a) Exothermic
   (b) Endothermic
   (c) Irreversible
   (d) Spontaneous process



Endothermic Reaction	Exothermic Reaction
Endothermic reactions are chemical reactions in which the reactants absorb heat energy from the surroundings to form products.	An exothermic reaction is a reaction in which energy is released in the form of light or heat.
The energy is absorbed from the surrounding into the reaction.	The energy is released from the system to its environment.
Energy in the form of heat.	Energy is released as heat, electricity, light or sound.
Melting ice, evaporation, cooking, gas molecules, and photosynthesis are a few examples.	Rusting iron, settling, chemical bonds, explosions, and nuclear fission are a few examples.

(1.) b

TRICK TO FIND WHETHER A REACTION IS ENDOTHERMIC OR EXOTHERMIC

In-order to find about a reaction, we must calculate Δng, which is change in number of moles of gaseous atoms. This will only work when the reaction is in **gaseous phase**.

So, Δng= number if gaseous atom moles in product – number of gaseous atom moles in reactant
If $\Delta ng > 0$, then reaction will be endothermic
If $\Delta ng < 0$, then reaction will be exothermic
For example: (1) $N_2(g) + 3H_2(g) \leftrightharpoons 2NH_3(g)$
now, $\Delta ng = 2 - (1+3) = 2-4$
$\Delta ng = -2$
Since Δng is less than 0, reaction will be exothermic.
(2) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
now, $\Delta ng = 2-(2+1) = 2-3 = -1$
$\Delta ng = -1$
Here Δng is less than 0, reactions will be exothermic.

- **Some Exceptions:** the general rule that decomposition reactions are always endothermic and combination reactions are always exothermic is a simplification of the more complex reality of chemical reactions. In reality; there are some exceptions to this rule:

- Endothermic decomposition reactions: while many decomposition reactions are indeed endothermic (requiring heat to proceed), some can be exothermic, particularly when the reactants are unstable and release energy upon breaking apart. For example, the decomposition of nitrous oxide (N_2O) into nitrogen and oxygen is exothermic, even though it involves the breaking of a bond.

  $$2N(g) + O_2(g) \rightarrow 2NO(g)$$

- Exothermic combination reactions: while many combination reactions are indeed exothermic (release heat), some can be endothermic, particularly when the reactants are highly reactive and require energy input to form a bond. For example, the combination of hydrogen and fluorine to form hydrogen fluoride is endothermic, as it requires energy input to overcome the strong repulsion between the two atoms.

  $H_2 + F_2 \rightarrow 2HF$

- Neutralization reactions: neutralization reactions involve the combination of an acid and a base to form salt and water. While these reactions are typically exothermic, they can be endothermic if the acid or base is particularly strong, and a large amount of energy is required to break the strong bonds between the molecules.

  $HCl + NaOH \rightarrow NaCl + H_2O$

- Combustion reactions are generally exothermic, meaning they release heat. However, there are some exceptions to this. For example, the combustion of hydrogen and oxygen in the fuel cell of a car is an endothermic reaction, meaning it absorbs heat. Additionally, certain fuels, such as hydrogen, can also undergo endothermic recombination reactions.

2.10 SOME REACTIONS IN SOLID AND LIQUID PHASE

- **Respiration:**

  $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ + energy

  In respiration, oxygen is utilized to break down glucose and energy is released which helps us to do our activities. That's why it's an exothermic reaction.

- **Photosynthesis:**

  $6CO_2 + 6H_2O \xrightarrow{Sunlight} C_6H_{12}O_6 + 6O_2$

  Here energy is provided by sun to make glucose. Since this requires energy, it is an endothermic reaction.

- **Decomposition of vegetable matter:**

  Generally, decomposition reaction is an endothermic because breaking down into smaller molecules requires a lot of energy, but here after decomposition of vegetable matter, heat releases so it is an exothermic reaction.

- **$2FeSO_4 \xrightarrow{Heat} Fe_2O_3 + SO_2 + SO_3$**

  Since it requires heat & thermal decomposition is happening, it is an endothermic reaction.

- **$2Mg + O_2 \rightarrow 2MgO$**

  Since this is an example of combination process & in that energy is released along with the product, so it's an exothermic reaction.

- **$Cao + H_2O \rightarrow Ca(oh)_2$**

Same as previous, this is also an exothermic reaction. We can also see it in real life when water is added to quicklime, a large amount of heat is evolved with a hissing sound and the container become warmer.

- **$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$**

  In this decomposition is happening, so it's an endothermic reaction.

2.11 FAST AND SLOW CHEMICAL REACTIONS

Different chemical reactions occur at different rates, and on the basis of that the chemical reactions are broadly divided into 3 categories:

- **Fast or instantaneous reactions**:

  These reactions are so fast that they occur as soon as the reactants are brought together. Generally, these reactions involve ionic species and thus known as ionic reactions. These reactions take about 10^{-14} to 10^{-16} seconds for completion. It is almost impossible to determine the rates of these reactions. Some such examples are:

  - ❖ Precipitation of AgCl, when solutions of silver nitrate and sodium chloride are mixed

    $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$
  - ❖ Precipitation of $BaSO_4$, when solutions of barium chloride and sulphuric acid are mixed

    $BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$
  - ❖ Neutralisation of an acid with a base when their aqueous solutions are mixed

    $HCl + NaOH \rightarrow NaCl + H_2O$

- **Slow reactions**:

  There are certain reactions which are extremely slow. They may take months together to show any measurable change at room temperature. It is also difficult to study the kinetics of such reactions. Some such examples are:

  (i) Reaction between hydrogen and oxygen at room temperature

  $2H_2 + O_2 \rightarrow 2H_2O$

  (this requires some minimum amount of energy to start the reaction and without it nothing will happen at room temperature).

  (ii) Reaction of atmospheric h_2s on basic lead acetate, this reaction gives blackening of white lead acetate paint which occurs very slowly.

  (iii) Reaction between carbon and oxygen at room temperature

  $C + O_2 \rightarrow CO_2$

  Carbon and oxygen are thermodynamically less stable than CO_2 at 298 k, yet coke does not spontaneously catch fire in air and remains unreacted even for years.

  (iv) Rusting of iron occurs very slowly

  $Fe_2O_3 + xH_2O \rightarrow Fe_2O_3.xH_2O$ (hydrated ferric oxide)

- Moderate reactions:

  Between the above two extremes, there are a number-of reactions which take place at moderate and measurable rates at room temperature. Mostly these reactions are molecular in nature. Some common examples are:

(i) Decomposition of hydrogen peroxide

$2H_2O_2 \rightarrow 2H_2O + O_2$

(ii) Reaction between nitrogen dioxide and carbon monoxide

$NO_2 + CO \rightarrow NO + CO_2$

(iii) Reaction between nitric oxide and chlorine

$NO + Cl_2 \rightarrow NOCl_2$

(iv) Hydrolysis of an ester

$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

ester sodium acetate

1. The mechanism for the formation of $NOBr_{(g)}$ is [Raj ACF 2018]

$NO_{(g)} + Br_{2(g)} \rightleftharpoons NOBr_{2(g)}$

$NOBr_{2(g)} + NO_{(g)} \xrightarrow{RDX} 2NOBr_{(g)}$

Find the order of the reaction with respect to $NO_{(g)}$

(a) 3
(b) 0
(c) 1
(d) 2

2. The zero-order rate constant is expressed by the unit [Raj ACF 2018]

(a) $L\ mol^{-1}$
(b) $L\ mol^{-1}s^{-1}$
(c) $L^{-1}mol^{-1}s^{-1}$
(d) $L^{-1}mol\ s^{-1}$

3. The $t_{1/2}$ of reaction is doubled as the initial concentration of the reactant is doubled. What is the order of the reaction? [Raj ACF 2018]

(a) 3
(b) 2
(c) 1
(d) 0

4. For the first order reaction, the time required for 99.9% completion of reaction is how many times that required for 50% completion? [Raj ACF 2018]

(a) 50 times
(b) 10 times
(c) 5 times
(d) 2.5 times

5. The rate of reaction is expressed in different ways as follows: [CG Vyapam RFO 2021]

$$\frac{1}{2}\frac{\Delta[C]}{\Delta t} = -\frac{1}{3}\frac{\Delta[D]}{\Delta t} = \frac{1}{4}\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{\Delta t}$$

The reaction is

(a) 4A + B = 2C + 3D
(b) B + 3D = 4A +2C
(c) A + B =C + D
(d) 2C + 4A = B +3D

6. The rate constant of nth order reaction has unit its unit as [CGPSC ACF 2020]

(a) $Litre^{1-n}mol^{1-n}sec^{-1}$
(b) $Mol^{n-1}litre^{n-1}sec^{-1}$
(c) $Mol^{1-n}litre^{n-1}sec^{-1}$
(d) $Mol^{n-1}litre^{1-n}sec^{-1}$

7. For a reaction $\frac{1}{2}A \rightarrow 3B$, rate of disappearance of reactant 'A' is related to

the rate of appearance of product 'B' by the expression: [CGPSC ACF 2020]

(a) $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$

(b) $-\frac{d[A]}{dt} = \frac{6d[B]}{dt}$

(c) $-\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$

(d) $-\frac{d[A]}{dt} = \frac{1}{6}\frac{d[B]}{dt}$

8. The decomposition reaction of ammonia gas on platinum surface has a rate constant, $k=2.5 \times 10^{-4}$ mol L^{-1} s^{-1}. The order of the reaction is [CGPSC ACF 2020]

(a) Zero order

(b) First order

(c) Second order

(d) Fractional order

9. What is the unit of second order reaction? [MPPSC SFM SP 2019]

(a) S^{-1}

(b) $Mol^{-1}L\ s^{-1}$

(c) Mol L^{-1} s^{-1}

(d) Mol^{-2} L s^{-1}

10. For a chemical reaction R → P, rate of reaction is given by [MPPSC SFS Main 2019]

(a) $\frac{\Delta[R]}{\Delta t}$

(b) $\frac{-\Delta[R]}{\Delta t}$

(c) $-\frac{\Delta[R]}{\Delta t}$

(d) $\frac{\Delta[P]}{\Delta[R]}$

11. The reaction A → product is zero order while reaction B→ product is first order reaction. for what initial concentration of A, the half-lives of two reactions are equal? [CG pariyojna 2021]

(a) $Log_e 4M$

(b) $\frac{1}{2} log_e 2M$

(c) $log_e 2M$

(d) $4\ log_e 2M$

Answer Key
(1.) d, (2.) d, (3.) d, (4.) b, (5.) b, (6.) c, (7.) d, (8.) a, (9.) b, (10.) c, (11.) a

CHAPTER

3

ACIDS, BASES & PH SCALE

Syllabus: properties and uses of acids & bases, different concepts of acids & bases (Arrhenius, Bronsted-Lowry, Lewis), conjugate acids & bases, HSAB concept, pH discovery, pH of acids, bases & water, dissociation constant

3.1 INTRODUCTION

The word Acid comes from a Latin word ‘Acidus’ which means ‘sour.’ An acid is any hydrogen-containing substance, capable of donating a proton (hydrogen ion) to another substance. A base is a molecule or ion, able to accept a hydrogen ion from an acid.

Acidic substances are usually identified by their sour taste. They are known to turn blue litmus paper into red and liberate dihydrogen on reacting with some metals.

Bases on the other hand, are characterized by a bitter taste and a slippery texture. A base that can be dissolved in water is referred to as an alkali. Bases are known to turn red litmus paper blue and feel soapy.

3.2 PROPERTIES OF ACIDS

(1) Acids are corrosive in nature.

(2) They are good conductors of electricity.

(3) Their pH is always less than 7.

(4) Examples: Sulfuric acid(H_2SO_4), Hydrochloric acid (HCl), Acetic acid (CH_3COOH).

3.3 PROPERTIES OF BASES

(1) In their aqueous solutions, bases act as good conductors of electricity.

(2) Their pH value is always greater than 7.

(3) Bases release hydroxide ions (OH^-) when dissolved in water.

(4) Example: Sodium Hydroxide (NaOH), milk of magnesia [$Mg(OH)_2$], calcium hydroxide [$Ca(OH)_2$].

3.4 USES OF ACIDS & BASES

(1) **Acids:**

- A diluted solution of acetic acid, called vinegar, has various household application, and it primarily used as food preservative.
- Sulphuric acid (H_2SO_4) is widely used is batteries. The batteries used to start the engines of automobiles commonly contain this acid.
- Citric acid is an integral part of lemon juice and orange. it can also be used as food preservative.
- The industrial production of explosives, dyes, fertilizers, and paints involves the use of nitric acid and sulphuric acid.
- Phosphoric acid is a key ingredient in many soft drinks.

(2) **Bases:**

- The manufacturing of soap and paper involves the use of sodium hydroxide (NaOH). It is also used in manufacturing of rayon.
- $Ca(OH)_2$, also known as slaked lime or calcium hydroxide , is used to manufacture bleaching powder ($CaOcl_2$).
- Dry mixes used in painting or decoration are made with the help of calcium hydroxide [$Ca(OH)_2$].
- Milk of magnesia [$Mg(OH)_2$] is commonly used a laxative. It also reduces any excess acidity in the human stomach and therefore it is used as an antacid.
- Ammonium hydroxide is a very important reagent used in laboratories.
- Any excess acidity in solids can be neutralized by employing slaked lime.

3.5 SOME CONCEPTS REGARDING ACIDS AND BASES

➢ **Arrhenius concept of Acids & Bases:** The Swedish scientist Svante Arrhenius defined acids as substance that dissociates in water to give hydrogen ions $(H^+)_{aq}$. Example- nitric acid (HNO_3) and hydrofluoric acid (HF) etc. These protons go on to form hydronium ions (H_3O^+) by combining with water molecules. And the Bases are substances that produce hydroxyl ion $(OH^-)_{aq}$. example sodium hydroxide (NAOH), calcium hydroxide [$Ca(OH)_2$] etc. The strength of an acid or base depends upon its tendency to furnish H^+ or OH^- ions in solution.

- **Merits:** One of the merits of this theory is that it successfully explains the reaction between acids & bases that yield salts & water.
- **Limitation:** An important limitation of this concept is that it fails to explain how substances lacking hydroxide ions from basic solution dissolved in water, such as No_2^- and F^-.

Another limitation of this is being applicable only to aqueous solutions.

The ionization of an acid $HX_{(aq)}$ can be represented by the following equations:

$$HX_{(aq)} \rightarrow H^+_{(aq)} + X^-_{(aq)}$$

or

$$HX_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + X^-_{(aq)}$$

Here a bare proton, H^+ is very reactive and cannot exist freely in aqueous solutions, thus it bonds to the oxygen atom of water and give hydronium ion (H_3O^+). Similarly, a base molecule like MOH ionizes in aqueous solutions according to the equation:

$$MOH_{(aq)} \rightarrow M^+_{(aq)} + OH^-_{(aq)}$$

➢ **Bronsted-Lowry concept of Acids & Bases:**

According to Bronsted – Lowry theory, Acid is a substance capable of donating a proton (H^+ ion). Bronsted acid undergo dissociation to yield protons and therefore increases the concentration of H^+ ion in the solution. A Base is defined as substance capable of accepting a proton (H^+ ion).

- **Merit:**

  An advantage of this theory is its ability to explain the acidic or basic nature of ionic species.
- **Limitation:**

  An important limitation of this theory is that it fails to explain how compounds lacking hydrogen exhibit acidic property, such as BF_3 and $AlCl_3$.

A base is defined as substance capable of accepting a proton (H^+ ion)

For example:

The dissociation of NH_3 in H_2O represented by the following equation:

$NH_3(aq) + H_2O(l) \leftrightharpoons NH_4(aq) + OH^-(aq)$

(Base) (Acid) (Conjugate acid) (conjugate base)

The basic solution is formed due to the presence of hydroxyl ions. In this reaction, water molecule acts as proton donor and ammonia molecule acts as proton acceptor and thus, they are called Bronsted – Lowry acid and base, respectively.

Conjugate Acids and Bases:

In above reaction, when reverse is taken, H^+ (proton) is transferred from $NH4^+$ to OH^-. In this case NH_4^+ acts as Bronsted acid while OH^- acts as Bronsted base. The acid–base pair that differs only by one proton is called a conjugate acid – base pair.

Therefore, OH^- is called the conjugate base of an acid H_2O and NH_4^+ is called conjugate acid of the base NH_3.

Acid + Base ⇋ Conjugate base + Conjugate acid

Example:

$$CH_3COOH + H_2O \leftrightharpoons CH_3COO^- + H_3O^+$$

In above reaction acid: CH_3COOH, base: H_2O, conjugate acid: H_3O^+, conjugate base: CH_3COO^-

Note: Conjugate acid forms by adding H^+ ion to base, conjugate base forms by removing H^+ ion from acid.

Lewis Acids & Bases:

The Lewis definition of an acid states that it is a species that has a vacant orbital and therefore, has ability to accept a lone electron pair. On the other hand, Lewis-base is a species that holds a lone pair of electrons and therefore, can act as an electron – pair donor. This theory does not involve the hydrogen atom in its definition of acids and bases.

- Lewis-acids are electrophilic in nature whereas Lewis bases possess nucleophilic qualities.
- Examples of Lewis acids: Cu^{2+}, BF_3, Fe^{3+}. Example of Lewis bases: F^-, NH_3, and C_2H_4(ethylene).
- A Lewis acid accepts an electron pair from a Lewis base, forming a co-ordinate covalent bond in the process. The resulting compound is referred to as a Lewis adduct.

Advantage:

Many compounds can be defined as acids or bases by it. However, it offers little insight into the strength of these acids and bases.

Limitation:

It fails to explain the acid- base reactions that do not involve the formation of a co-ordinate covalent bond.

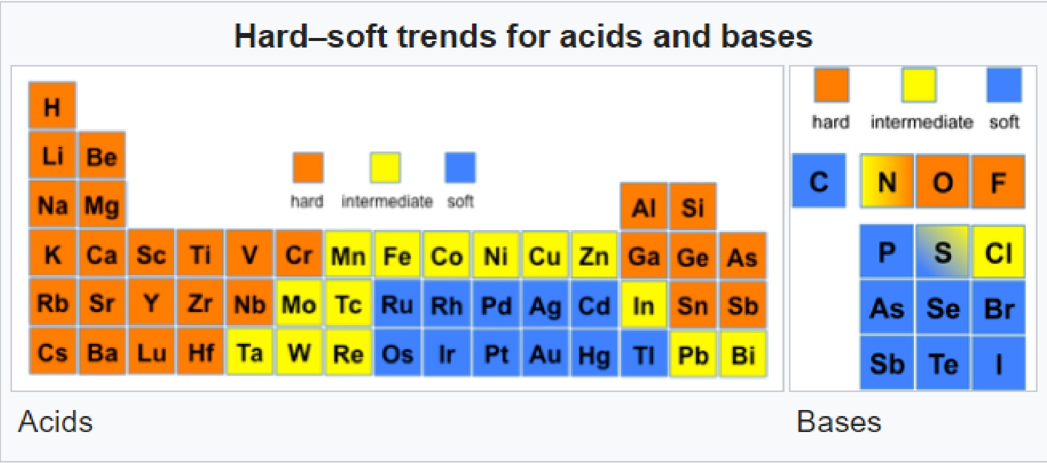
Hard & soft acid/base concepts: it is also known as **HSAB concept**. Its intention is to identify the product of Lewis acid-base reactions that have greatest stability. This concept states that: “soft acids react faster and form stronger bonds with soft bases, whereas hard acids react faster and form stronger bonds with hard bases, all other factors being equal.” The classification in the original work was mostly based on equilibrium constants for reaction of two Lewis bases competing for a Lewis acid.

Hard acids & bases: Hard **acids** consist of small highly charged cations and molecules in which a high positive charge can be induced on the central atom. Examples of Hard Acids: H^+, Li^+, K^+, Ca^{2+}, Al^{3+}, Sn^{4+}, BF_3, BCl_3, CO_2, RCO^+, SO_3, RMgX, VO_2^+, $AlCl_3$.

Hard **bases** are highly electronegative and of low polarizability. Hard bases react more readily to form stable compounds and complexes with hard acids. Examples of Hard Bases: F^-, OH^-, NH_3, N_2H_4, ROH, H_2O, SO_4^{2-}, PO_4^{3-}, CO_3^{2-}, CH_3COO^-

Soft acids & bases: Soft **acids** consist of large low charge cations and molecules with relatively high energy occupied molecular orbitals. Soft acids are readily polarizable. Examples of Soft Acids: Cs^+, Cu^+, Au^+, Pt^{2+}, Hg^+, BH_3, Br_2, I_2, RO^+, quinones. Soft **bases** have low electronegative and high polarizability. Examples of Soft Bases: H^-, R^-, CO, PR_3, C_6H_6, SCN^-, I^-, S^{2-}.

ACID		**BASE**	
Hard acid	Soft acid	Hard base	Soft base
Hydronium (H_3O^+)	Mercury (CH_3Hg^+, Hg^{2+}, Hg_2^{2+})	Hydroxide (OH^-)	Hydride (H^-)
Alkali metals (Li^+, Na^+, K^+)	Platinum & palladium (Pt^{2+}, Pd^{2+})	Alkoxide (RO^-)	Thiolate (RS^-)
Titanium & chromium (Ti^{4+}, Cr^{3+}, Cr^{6+})	Gold & silver (Au^+, Ag^+)	Halogens (F^-, Cl^-)	Halogens (I^-)
Boron trifluoride (BF_3)	Borane (BH_3)	Ammonia (NH_3)	Phosphine (PR_3)
Carbocation (R_3C^+)	P-chloranil ($C_6Cl_4O_2$)	Carboxylate (CH_3COO^-)	Thiocyanate (SCN^-)
Lanthanides (Ln^{3+})	Bromine & iodine (Br_2, I_2)	Carbonate (CO_3^{2-})	Carbon monoxide (CO)
Thorium, uranium (Th^{4+}, U^{4+})		Hydrazine (N_2H_4)	Benzene (C_6H_6)


Hard–soft trends for acids and bases

Note:

- The increasing electronegativity affects the acidic strength positively. If the central atom is highly electronegative, then it pulls electron, polarizes the bond, and make the molecule more stable. **But** HCl is more acidic than HF. This happens because for elements in the same group in the periodic table, the bond strength dominates over the polar nature. For example, the acidity order of group 17 hydrides is HF<HCl<HBr<HI. For elements along the same period, however the polarity determines the acidic strength. Hence acidic strength order for period 2 hydrides is CH4<NH3< H2O<HF.

- The strength of the carboxylic acids is known to vary based on the total power to withdraw electrons of the atoms that are bonded to the carboxyl group. When the substituent group has more electron withdrawing power, the stronger will be the acid. The acidic strength is decreased by the electron releasing group. For example, (although all are weak acids), the CH_3 group has a lesser electron withdrawing power than H. So, CH_3COOH is comparatively weaker acid than HCOOH. The correct order of acidic strength is-
  $HCOOH > CH_3COOH > CH_3CH_2COOH > CH_3CH_2CH_2COOH$

Questions:

1. Among the following, which one is not a Lewis-acid? [MPPSC SFS Main 2020]
   (a) BF_3
   (b) SO_3
   (c) CaO
   (d) Ag^+
2. Which of the following is most acidic? [Raj ACF 2018]
   (a) CH_4
   (b) NH_3
   (c) H_2O
   (d) HF
3. Which of the following oxide of nitrogen is not acidic? [Raj ACF 2018]
   (a) N_2O
   (b) N_2O_3
   (c) NO_2
   (d) N_2O_5
4. Which of the following is Lewis-base? [CGPSC ACF 2017]
   (a) Cu^{2+}
   (b) BF_3
   (c) Ni
   (d) CO
5. Which of the following statement is correct? [CGPSC ACF 2017]
   (a) CH_4 is more acidic than NH_3
   (b) HF is more acidic than HI
   (c) HCl is more acidic than HBr
   (d) HF is more acidic than HCl
   (e) None of these
6. Such substance which behaves as both acid and base are called [CGPSC ACF 2017]
   (a) Strong acid
   (b) Weak acid
   (c) strong base
   (d) amphoteric substance
   (e) none of these
7. Which one of the following species is amphoteric in nature? [CGPSC ACF 2020]
   (a) H_3O^+
   (b) Cl^-
   (c) HSO_4^-
   (d) CO_3^{2-}
8. According to Bronsted – Lowry concept, acids are: [CGPSC ACF 2020]
   (a) Proton donors
   (b) Electron donors
   (c) Proton acceptors
   (d) Electron acceptors
9. Conjugate base of HCO_3^- is [CGPSC ACF 2020]
   (a) H_2CO_3
   (b) CO_3^{2-}
   (c) H^+
   (d) CO_2
10. Oxidation of which of the following substance will yield a stronger acid? [MH Forest service Main 2019]
   (a) H_2CO_3
   (b) HNO_3

(c) HIO

(d) H_4SiO_4

11. Which of the following is amphoteric in nature? [MPPSC SFM 2018]

(a) H_2O

(b) HCl

(c) NaOH

(d) HNO_3

12. According to Lewis concept of acid – bases, Lewis-acid are [MPPSC SFM 2018]

(a) Proton accepters

(b) Proton donors

(c) Electron pair accepters

(d) Electrons pair donor

13. Which among the following is strongest acid? [MPPSC SFM 2018]

(a) HCOOH

(b) CH_3COOH

(c) CH_3CH_2COOH

(d) $CH_3CH_2CH_2COOH$

14. which of the following is not a soft base? [MPPSC SFM SP 2019]

(a) S^{-2}

(b) I^-

(c) CO_3^{2-}

(d) SCN^-

15. Which of the following is/are examples of oxoacids? [MPPSC SFM SP 2019]

(a) Hypochlorous acid

(b) Hydrochloric acid

(c) Both (a) and (b)

(d) None of these

16. H_2O and CO_2 are? [MPPSC SFM SP 2019]

(a) Hard acid and hard base

(b) Soft acid and hard base

(c) Soft acid and soft base

(d) Hard base and soft acid

17. Which statement is not correct? [MPPSC SFS Main 2021]

(a) Acids are sour in taste and change the colour of blue litmus to red

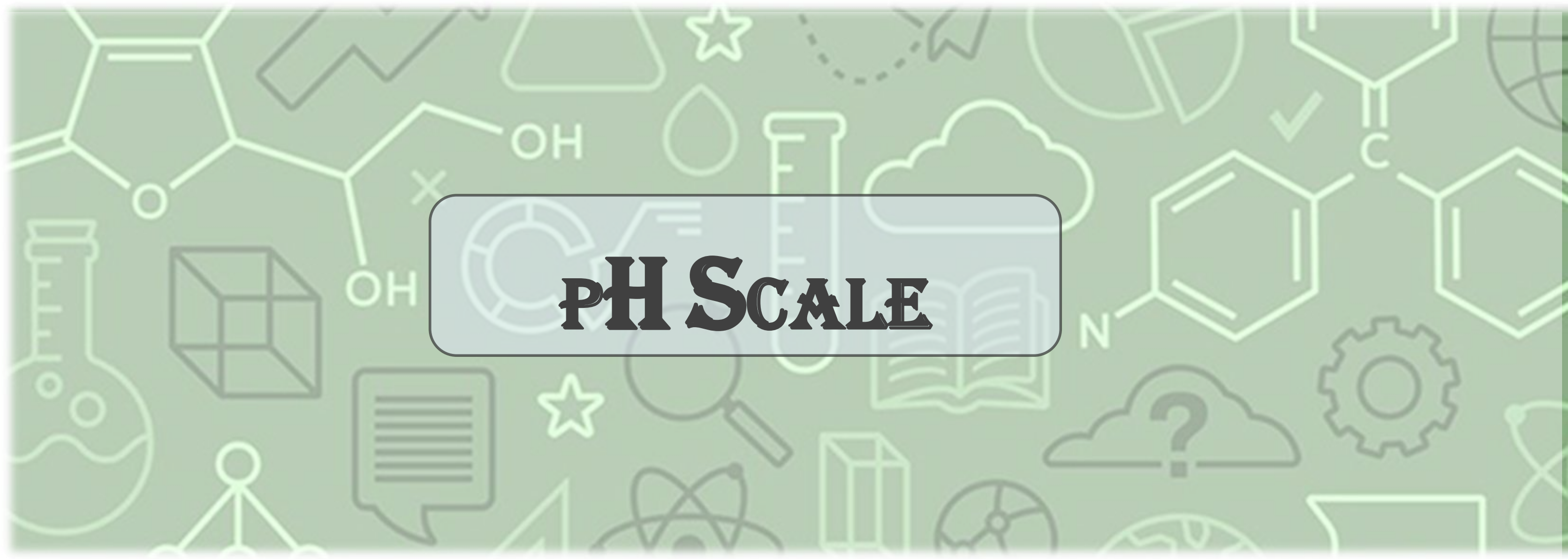
(b) Acids are sour in taste and change the colour of red litmus to blue

(c) Bases are bitter and change the colour of red litmus to blue

(d) Litmus is a natural indicator

Answer Key

1. c	2. d	3. a	4. d	5. e	6. d	7. c	8. a	9. b	10. b	11. a	12. c
13. a	14. c	15. c	16. c	17. b							



pH SCALE

3.6 INTRODUCTION

pH is defined as the negative logarithm of hydrogen (H^+) ion concentration. In other word, hydronium ion concentration expressed on a logarithmic scale known as the pH scale. As all the acids and bases do not react with the same chemical compound at the same rate. Some react very vigorously, some moderately, while some show no reaction. To determine this and the strength of acids and bases, we use a universal indicator and that is called pH.

The pH scale is logarithmic, meaning that an increases or decreases of an integer value changes the concentration by a tenfold, for example a pH of 3 is ten times more acidic than a pH of 4 and likewise a hundred times more acidic than a pH of 5. Similarly, a pH of 11 is ten times more basic than a pH of 10.

3.7 DISCOVERY

In 1909, Sorensen introduced the concept of pH as a way of expressing acidity & basicity. Mathematical Expression of pH:

pH is expressed as:

$pH = -\log_{10}[H^+]$

and $[H^+] = 10^{-pH}$

Similarly, pOH is expressed as:

$pOH = -\log[OH^-]$

Now, at 298K, ionic product of water Kw can be given as:

$Kw = [H^+][OH^-] = 10^{-14}$

Taking the negative log of RHS AND LHS:

$-\log Kw = -\log[H^+.OH^-] = -\log 10^{-14}$

Or $pKw = -\log[H^+] – \log[OH^-] = 14$ $[\log_{10}10 = 1]$

$pKw = pH + pOH = 14$

3.8 pH of ACIDS And BASES

At room temperature solutions having a value of pH ranging from 0 to less than 7 are known as acidic and the pH from more than 7 to 14 are known as basic solutions. Solutions having the pH value of 7 are known as neutral solutions.

Acidic	Neutral	Basic
Less than 7	7	More than 7

- Solution having (0) pH= strong Acids
- Solution having (14) pH = strong Base

3.9 pH OF PURE WATER WHEN TEMPERATURE INCREASES

As temperature increases, the degree of dissociation of water increases. Thus, the water dissociates to give more [H^+] ions, hence its pH decreases. However, the nature of water remains neutral, even if its pH changes. At 100^0C, pH value of 6.14 is neutral point instead of 7.

Note:

- pH of strong acid or base does not depend upon the temperature.
- pH of weak acid decreases with increases in temp. due to increases in ionization.
- pH of weak base increases with increases in temperature due to increase in ionization or [OH^-] concentration.

Note: Dissociation constant: In chemistry an acid dissociation constant (also known as acidity constant, or acid-ionization constant) is a quantitative measure of the strength of an acid in solution. It is the equilibrium constant for a chemical reaction:

$HA \rightleftharpoons H^+ + A^-$

The chemical species HA is an acid that dissociates into A^-, the conjugate base of the acid and a hydrogen ion, H^+. The system is said to be in equilibrium when the concentrations of its components will not change over time, because both forward and backward reactions are occurring at the same rate.

The dissociation constant is defined by:

$K_a = \frac{[H^+][A^-]}{HA}$

For example: The pH of 0.10 M solution of weak monoprotic acid 4.0, The dissociation constant of acids?

Solve: as we know $K_a = \frac{[H^+][A^-]}{HA}$

And for weak acid, [H^+] = [A^-]

So, $K_a = \frac{[H^+]^2}{[HA]} = \frac{[10^{-4}]^2}{0.1} = 10^{-7}$

3.10 Some pH examples

(1) Calculate the pH of a 0.200M HCl solution?

Solve: Since HCl solutions are strong acids, so we can already expect a pH of less than 7.

From the formula:

$pH = -\log[H^+]$

$= -\log(0.200)$

pH = 0.70 ………… Ans.

(2) What is the hydrogen ion concentration of a solution that has a pH of 4.30?

Solve: $pH = -\log[H^+]$

$4.30 = -\log[H^+]$

So, $[H^+] = 10^{-4.30}$ $[H^+ = 10^{-pH}]$

$[H^+] = 5.01 \times 10^{-5}$ M…………………….Ans.

(3) The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3}M, what is its pH & pOH?

Solve: $pH = -\log[H^+]$

$= -\log(3.8 \times 10^{-3})$

= -[log(3.8) + log(10^{-3}) [log(m.n)=log m+log n]

= -log3.8 – log10^{-3}

= -0.58 + 3

pH = 2.42………Ans.

(4) Calculate the pOH of a solution with [OH^-] concentration of 5.23 x 10^{-5} M?

Solove: pOH = -log [OH^-]

=-log(5.23 x 10^{-5})

= 4.20…………… Ans.

(5) What is the pOH of a solution that has a [H^+] of 0.100M Hcl?

Solve: First calculate the pH value and then use that to calculate pOH:

So, pH = -log[H^+]

pH =-log[0.100] =1

Now, we know

pH + pOH = 14

pOH = 14 -1

=13……….Ans.

(6) Calculate the pH and pOH of a solution having [H^+] concentration of 10^{-2}M?

Solve: As we know

[H^+] = 10^{-2}

And pH =-log[H^+] =-log [10^{-2}]

pH = 2log10

pH = 2 [log10= 1]

Now , pH + pOH = 14

So , pOH = 14-2

pOH = 12……... Ans.

(7) Calculate the pOH of 0.1N NaOH solution? [CG ACF 2017]

Solve: NaOH → Na^+ + OH^-

Since, [OH^-] = 0.1N

pOH = -log[OH^-]

=-log[10^{-1}] [0.1 = 10^{-1} = 1/10]

pOH = 1

Now, pH + pOH = 14,

pH = 14 – 1 = 13…………….Ans.

(8) Calculate the pH of a 1.0 x 10^{-8} M solution of HCl?

Solve: As we know that pH value of an acid solution is below 7. But in this question if we apply the logarithmic formula, we get 8 as an answer, which is completely wrong. Hence the answer would be 7 for pH & pOH both.

Note:

- If concentration of acid [H^+] is less than 10^{-7} and
- If concentration of Base [OH^-] is less than 10^{-7}

Then the pH will always be taken as 7.

(9) Calculate the pH & pOH of 10^{-3}M H_2SO_4 solution?

Solve: Here the molarity of H_2SO_4 is given, So, we must keep that in mind while solving the question.

$1\ H_2SO_4 \rightarrow \quad 2H^+ \quad + 1SO_4^{-2}$

10^{-3}M $\quad$ 2 x 10^{-3}M $\quad$ 10^{-3}M

Now, while calculating the pH, we take the concentration of $[H^+]$ as 2 x 10^{-3} because the $[H^+]$ ion has 2 moles.

Solve: pH =-log $[H^+]$

= -log[2 x 10^{-3}] $\quad$ [log(m x n) = logm+ logn]

= -log2 – log10^{-3} $\quad$ [log10=1]

= -0.3010 +3

pH = 2.7 ……….Ans.

And pH + pOH = 14

pOH = 14 – 2.7

pOH = 11.3……….Ans.

(10) Calculate the pH of 0.001 M barium hydroxide, assuming that it is completely ionized?

Solve: $Ba(OH)_2$ ionizes in water as:

$Ba(OH)_2 \leftrightarrow Ba^{2+} + 2OH^-$, since it is completely ionized, one mole of barium hydroxide gives 2 moles of OH^- ions

Therefore, $[OH^-] = 2 \times 0.001 = 0.002$M

Now formula $[H_3O^+] = \frac{K_W}{[OH^-]} = \frac{1\times10^{-14}}{0.002} = 5\times10^{-12}$

Now, pH = $-\log[H_3O^+] = -\log[5\times10^{-12}]$

pH = – (log5 + log 10^{-12})

= – (0.699-12) = 11.30 …..Ans

Note: **Isoelectric point:** it is the pH at which a molecule carries no net electric charge or is electrically neutral in the statistical mean. The standard nomenclature to represent the isoelectric point is pH(I).

Questions:

1. Calculate the pH of 0.001 M barium hydroxide, assuming that it is completely ionized. Among the following, choose the correct answer: [MPPSC SFS Main 2020]
   (a) 11.0
   (b) 11.3
   (c) 12.0
   (d) 12.5
2. The pH of 0.1 N NaOH solution is [CGPSC ACF 2017]
   (a) 0.1
   (b) 13.9
   (c) 1
   (d) 13
   (e) None of these
3. The pH of pure water is changed on addition of CH_3COONa. It is [CGPSC ACF 2017]
   (a) > 7
   (b) < 7
   (c) Equal of 7
   (d) All of them correct
   (e) None of these
4. The pH at which there is no net charge on the protein molecules is [Raj ACF 2018]
   (a) Isoelectric point
   (b) Neutralization pH
   (c) Acidic pH
   (d) Basic pH
5. The hydrogen ion concentration in our stomach due to abundant HCl present in gastric juice is 0.01 mol/L. The pH of gastric juice is [Raj ACF 2018]
   (a) 1
   (b) 0.01
   (c) 2
   (d) 14
6. The pH of 0.1 M solution of weak monoprotic acid 4.0, The dissociation constant of acid is [CG Vyapam RFO 2021]
   (a) 1×10^{-10}
   (b) 1×10^{-4}
   (c) 1×10^{-7}
   (d) 1×10^{-5}
7. The pH of 0.05 molar solution of sulphuric acid is [CGPSC ACF 2020]
   (a) 1
   (b) 0
   (c) 4
   (d) 2
8. What is pH of 10^{-4}M NaOH solution? [MPPSC SFM 2018]
   (a) 4
   (b) 10
   (c) 7
   (d) 12
9. Calculate the pH of an aqueous ammonia solution that has OH^-concentration of 1.9×10^{-3}M? [MPPSC SFM SP 2019]
   (a) 11.28
   (b) 9.28
   (c) 7.28
   (d) 5.29
10. The pH value of 0.02M NaOH solution will be [MPPSC SFS Main 2019]
   (a) 05
   (b) 09
   (c) 02
   (d) 12

Answer Key

1. b	2. d	3. a	4. a	5. c	6. c	7. a	8. b	9. a	10. d

CHAPTER

4

CHEMICAL COMPOUNDS

Syllabus: water: properties and uses, hard & soft water, heavy water; Preparation, properties & uses of washing soda, baking soda, bleaching powder, plaster of Paris, gypsum; Preparation of building materials: lime, cement, glass, steel

4.1 WATER

- **Introduction:**

  Water the most abundant and essential substance on earth is often taken for granted. Yet its properties are truly remarkable and play a vital role in sustaining life. Its chemical formula is H_2O. One molecule of water has two hydrogen atoms covalently bonded to a single oxygen atom. The structure of water molecule is non-linear. 71% of earth is surrounded by water and 65% of human body is composed of water.

- **Physical properties:**

  Water is a colourless & tasteless liquid. The molecules of water have extensive hydrogen bonds resulting in high melting and boiling points. As compared to other liquids, water has a higher specific heat, thermal conductivity, surface tension, dipole moment etc. Water is an excellent solvent and therefore it helps in the transportation of ions and molecules required for metabolism. It has a high latent heat of vaporization which helps in the regulation of body temperature.

> The two reasons for high boiling point of water are –
>
> - Formation of H bonds, which requires more energy for breaking the 'extra' bonds.
> - Increase in *van der Waals* forces, as the result of which we need to supply more temperature for water to boil, or change from liquid state to vapour state.

- **Chemical Properties:**

  (1) **Amphoteric Nature:**

  Water can act both as acid and base, that's why it is called amphoteric.

  ❖ **Acidic Behaviour:**

  $H_2O(l) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

  ❖ **Basic Behaviour:**

  $H_2O(l) + H_2S(aq) \rightleftharpoons H_3O^+(aq) + HS^-(aq)$

  (2) **Redox Reaction:**

  Electro positive element reduces water to hydrogen molecule and this is called reduction.

Example: $2H_2O(l) + 2Na(s) \rightarrow 2NaOH(aq) + H_2(g)$

During the photosynthesis process, water is oxidized to O_2, hence water can be oxidized and reduced.

(3) **Hydrolysis Reaction:**

Water has a very strong hydrating tendency due to its dielectric constant. It dissolves many ionic compounds. Some covalent and iconic compounds can be hydrolysed in water.

(4) **Solvency of water:**

Water is described as the universal solvent. This is because of its high dielectric constant along with chemical composition.

Chemical formula	H_2O
Boiling Point	99.98^0C (373K)
Melting point	0.00^0C (273K)
Crystal structure	Hexagonal→ (Ice at atm pressure)
pH value	7
Conductivity	Pure water is bad conductor of electricity
Solubility	Poorly soluble in aliphatic and aromatic hydrocarbons, and ethers. Improved solubility in amines, ketones, alcohols, carboxylate. Partially miscible with bromine, ethyl acetate, diethyl ether.

- **Hard & Soft water:**

  According to WHO, water containing calcium carbonate at concentrations 60 – 120 mg/l is moderately hard, 120 – 180mg/l is hard and beyond that is very hard. The presence of minerals like calcium, magnesium and their sulphates, carbonates, bicarbonates, contributes towards the hardness of water. Hard water can be divided into:

  (1) **Temporary Hard water:**

  The water that contains carbonates and bicarbonate of calcium and magnesium is known as temporary hard water. This is also known as alkaline hardness and can be easily removed by boiling the water and/or Clark's method.

  (2) **Permanent Hard water:**

  The water that contains chlorides and sulphates of calcium and magnesium. It is also known as non-alkaline hardness and can be removed by some methods:

  - Treatment by Na_2CO_3 (washing soda)
  - Calgon's method ($Na_2P_6O_{18}$)
  - Ion exchange Method
  - Synthesis Resin Method

- **Soft Water:**

  It is defined as the water containing lower amount of minerals unlike calcium and magnesium. pure water or rain water considers as soft water.

Difference between Hard& Soft water:

Hard water	**Soft water**
If the water consists of higher concentrations of minerals, then it is classified as hard water.	If the water consists of lower concentrations of minerals such as magnesium, calcium then it is classified as soft water.
Hard water does not form lather or foam. And it leaves spots on the washed dishes after they dried.	Soft water forms lather and foam. And it does not leave any spots on dishes after they are dried.
Soap is not effective against hard water. And Hard water is preferred as drinking water.	Soap is effective against soft water. And Soft water is not preferred as drinking water.
Hard water may cause side effects on the skin, hair. Hair and skin may become dry due to hard water.	A Soft water does not cause any side effects on the skin, hair. Instead; hair and skin may become soft.
Hard water forms when water flows through limestone and chalk and other rocks.	Soft water is formed by passing hard water over an ion exchange resin.
Hard water has a characteristic taste and it isn't suitable for heavy machinery, boilers, and other appliances.	Soft water is known to have a salty taste and is widely suitable for machinery, boilers, etc.
Hard water is rich in minerals. Hence it mainly contains minerals such as magnesium and calcium.	Soft water is not rich in minerals. It mainly contains sodium ions.
Example: Water found in wells, groundwater	Example: rainwater

- **Heavy Water (D_2O):**

  Heavy water was discovered by Urey and co-workers in 1931-32.

  It is a compound that is made up of oxygen and deuterium, a heavier isotope of hydrogen. Heavy water is also called deuterium oxide and is denoted by chemical formula D_2O.

  - **Physical Properties:**
    - Heavy water has a colourless appearance at STP.
    - At room temperature, it exists as an odourless liquid.
    - Since the Density of D_2O is approximately 11% greater than that of H_2O, an ice cube made of deuterium oxide will sink in normal water.
    - It forms a homogeneous mixture when mixed with normal water.
  - **Chemical Properties:**
    - At given temperature the concentration of D^+ ions in a D_2O sample, is generally lower than H^+ ion in H_2O sample.
    - The isotopes of hydrogen exhibit different chemical behaviour because of the difference in their atomic masses.
  - **Method of preparation:**

    Heavy water is prepared by the prolonged electrolysis of water containing alkali.
    - Electrolyte: Water containing NaOH
    - Cathode: Steel Vessel
    - Anode: Nickel sheet with Holes

- **Uses of D_2O:**
  - It is used for the preparation of deuterium.
  - It is used as a moderator in the nuclear reactor to slow down the neutrons, so that the neutrons can react with U^{235} instead of U^{238}.

4.2 WASHING SODA (SODIUM CARBONATE):

Washing soda is a chemical compound with the formula $Na_2CO_3.10H_2O$. it is an inorganic hydrate of sodium carbonate. It was extracted from the plants growing in sodium rich soils and hence the name soda ash. It is white crystalline solid and a metal carbonate which is soluble in water.

- Na_2CO_3 → Soda Ash (Anhydrous Sodium Carbonate)
- $Na_2CO_3.H_2O$ → Crystal Carbonate
- $Na_2CO_3.7H_2O$ → Heptahydrate Sodium Carbonate

Note: Black ash is impure sodium carbonate produced in Le-Blanc method when salt cake is reduced buy coke. (Na_2CO_3 + CaS = Black ash)

$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2$

(Salt cake) + (coke)

$Na_2S + CaCO_3 \rightarrow Na_2CO_3 + CaS$

(Black ash)

- **Methods of preparation:**

(1) **Solvay Process:**

This process has following steps.

- **Purification of Brine:**

  A highly concentrated solution of common salt is known as brine solution. Impurities like calcium, magnesium of brine are removed by the precipitation process. After filtration, brine is mixed with ammonia in the ammonia tower and the tower gets cooled.

- **Formation of sodium bi-carbonate:**

  In a carbonate tower, Carbon dioxide is passed through an ammoniated brine solution.

  $NH_3(aq) + CO_2(g) + Nacl(aq) + H_2O \rightarrow NaHCO_3(s) + NH_4Cl(aq)$

- **Formation of Sodium carbonate:**

  Sodium bi-carbonate is heated to 300⁰C to get Sodium carbonate.

  $2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$

  Anhydrous Sodium carbonate (soda Ash)

  $Na_2CO_3 + 10H_2O \rightarrow Na_2CO_3.10H_2O$

  Washing soda

- **Recovery of ammonia:**

  Ammonia can be recovered by treating the solution of ammonium chloride (NH_4Cl) with calcium hydroxide. This ammonia is again used in the Solvay process and calcium chloride is obtained as a by-product.

  $2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + 2H_2O$

(2) **Electrolytic process:**

In this process the breaking down of a compound in solution into its elements by means of an electric current, is used to bring about a chemical change. Electrolysis of sodium hydroxide (NaOH) gives us sodium carbonate. Nelson cell is used this process.

$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$

Properties:

(i) Physical:

- It is a white crystalline solid.
- It exists as a monohydrated salt ($Na_2CO_3.H_2O$) anhydrous salt, heptahydrate and decahydrate.
- It is soluble in water with heat and show alkaline nature due to hydrolysis.

  $Na_2CO_3 + 2H_2O \rightarrow 2NaOH + H_2CO_3$

(ii) Chemical:

- It has a high melting point of 851^0C.
- Reaction with silica:

  $Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3$(Sodium silicate) + $CO_2 \uparrow$
- Reaction with CO_2:

  $Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$ (sodium Bicarbonate)
- Reaction with impurities of hard water:

  $Na_2CO_3 + CaSO_4 \rightarrow CaCO_3 + Na_2SO_4$
- it gives pink colour with phenolphthalein and yellow with methyl orange.
- The aqueous solution of sodium carbonate is alkaline in nature because when it is dissolved in water, it gets hydrolysed and forms a strong base (sodium hydroxide) and a weak acid (carbonic acid):

  $Na_2CO_3 + 2H_2O \rightarrow H_2CO_3 + 2NaOH$

Uses:

- Sodium Carbonate is used as a cleansing agent in industries and household.
- It finds its application in manufacturing of glass, sodium silicate, paper, caustic soda, soap, powders.
- It is one of the most important agents in laundries, that is why it is called washing soda.
- In petroleum and textile industry.

4.3 BAKING SODA (SODIUM HYDROGEN CARBONATE):

Sodium bicarbonate also known as baking soda is a chemical compound with the formula $NaHCO_3$ and the IUPAC designation sodium hydrogen carbonate. A sodium cation (Na^+) and a bicarbonate anion (HCO_3^-) combine to form this salt. It is a white crystalline substance that is commonly found as a fine powder. It tastes slightly salty and alkaline.

- **Preparation:**
  - Solvay process is used for production of sodium bi-carbonate industrially. In this process carbon dioxide, water, ammonia, and brine solution (in concentrated form) are used as raw materials.

    $CO_2 + H_2O + NH_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$

    (sodium Bicarbonate)

    Further in the process, we can obtain sodium carbonate.
  - Laboratory method: In lab sodium bicarbonate is produced by sodium carbonate.

    $Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$
- **Properties:**
  - It is a white, odourless, crystalline solid.
  - It is non-flammable.

- ❖ Powder dust is not explosive.
- ❖ It has a melting point of 50^0C.
- ❖ It gives yellow colour with methyl orange and gives no colour with Phenolphthalein.
- ❖ After reacting with bases like Sodium hydroxide, it gives carbonates.

  $NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O$
- ❖ Reaction with acetic acid (present in vinegar):

  $NaHCO_3 + CH_3COOH \rightarrow CH_3COONa + H_2O + CO_2$

  It gives sodium acetate, water, and carbon dioxide

- **Uses:**
  - ❖ Reduces the acidity in the stomach as it acts as an antacid.
  - ❖ Used in baking industry as carbon dioxide is generated (due to the decomposition of $NaHCO_3$) which helps in raising of the dough.
  - ❖ It is used in eardrops, cosmetic and personal care products.
  - ❖ For production of Carbon dioxide.
  - ❖ Used in Fire Extinguishers, due to formation of soapy foam.
  - ❖ Acts as a pesticide.
  - ❖ Used in the process of washing as a water softener.
  - ❖ Used in making effervescent drinks.
  - ❖ It is used in a process for removing paint and corrosion called soda blasting (cleaning agent).
  - ❖ It is used in personal hygiene products like mouthwashes because it is effective against bacteria.

Note: Difference between baking soda & baking powder:

Baking Soda	Baking Powder
It has only one ingredient – sodium bicarbonate.	It consists of many ingredients, including bicarbonates (typically baking soda), and acid salts.
It does not contain monocalcium phosphate.	It contains monocalcium phosphate, which reacts with NaHCO3 when wetted and heated.
It reacts immediately with acids.	It does not immediately react when exposed to acids.
Short leavening process.	The leavening process is extended with the help of a second acid.
Baking products formed when baking soda is used are not as fluffy when compared to baking powder products, due to shorter reaction duration.	It gives fluffier products from baking.

4.4 BLEACHING POWDER:

Bleaching powder, also called Calcium Hypochlorite or calcium Oxychloride, is a chemical compound which is used for various purposes, majorly for its bleaching action. It is also known as chloride of lime. It is an ionic compound that is made up of a calcium cation (Ca^{+2}) and two hypochlorite anions (ClO^-). Despite being quite stable at room temperature, it slowly decomposes in moist environments, giving it a characteristic 'chlorine' smell. The oxidation done by nascent oxygen is responsible for bleaching nature.

- **Preparation:**

  The manufacturing of bleaching powder is carried out in Bachmann's plant. In this slaked lime reacts with chlorine gas and gives bleaching powder.

  $Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 + H_2O$

  (Bleaching powder)

  The solution of bleaching powder appears milky because some lime is still present there.

- **Properties:**

  (i) Physical:

  - Bleaching powder is a pale yellowish powder that possesses a strong smell of chlorine.
  - It is partially soluble in water, because of impurities, it can't dissolve completely in water.

  (ii) Chemical:

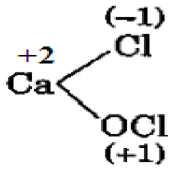
  - It performs a reaction with dilute acid to produce chlorine:

    $CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + Cl_2 + H_2O$
  - It reacts with carbon dioxide to produce chlorine:

    $CaOCl_2 + CO_2 \rightarrow CaCO_3 + Cl_2$
  - It acts as a strong oxidising agent:

    $CaOCl_2 + 2FeSO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + CaCl_2 + H_2O$
  - pH of bleaching powder is 11, thus it is basic in nature.

Note: oxidation state of chlorine: in bleaching powder [Ca(OCl)Cl], the two Cl atoms are in different oxidation states. One Cl^- having oxidation number of [-1] and the other as OCl^- having oxidation number of [+1].



- **Uses:**
  - Used as an oxidising agent in chemical industries. Bleaching happens due to this oxidation property.
  - Used for disinfection of water.
  - Used for bleaching washed clothes in the laundry.
  - Used as a bleaching agent in the textile industry for bleaching cotton and linen.
  - Used for making of chloroform.
  - It makes wool unshrinkable.

4.5 PLASTER OF PARIS:

Plaster of Paris is a popular chemical substance that is used mostly for sculpting materials and in gauze bandages. Known since ancient times, plaster of Paris is so called because of its preparation from the abundant gypsum found near Paris. It generally does not shrink or crack when dry, making it an excellent medium for casting moulds. In medieval and renaissance times, gesso (usually made of P.O.P. mixed with glue) was applied to wood panels, plaster, stone, or canvas to provide the ground for tempera and oil painting. It is also referred to as gypsum plaster. The chemical formula of P.O.P. is $[CaSO_4.\frac{1}{2}H_2O]$.

- **Preparation:**

P.O.P. is prepared from the chemical compound- monoclinic calcium sulphate dihydrate, which is also known as gypsum. By heating the gypsum at a very high temperature of about 100^0-120^0C, Approximately three-fourth of its water is lost, forming POP (calcium sulphate hemihydrate).

$$CaSO_4.2H_2O \xrightarrow{\Delta} \underset{[POP]}{CaSO_4.\frac{1}{2}H_2O} + 1\frac{1}{2}H_2O \text{ (discharged as steam)}$$

Since the presence of moisture may slow down the setting of plaster by bringing about the hydration process. Therefore, it is stored in moisture-proof containers.

- **Properties:**
    - POP is a white coloured powder, that forms crystals of gypsum when mixed with water.
    - When it is heated at 200^0C, forms an anhydrous calcium sulphate, also known as dead burnt plaster.
    - It expands slowly and slightly upon setting, so it is highly fire – resistant.
    - It is easy to spread on any surface and easy to level.
    - The exothermic setting process can be catalysed by sodium chloride. POP is retarded by alum or borax.
    - Mixture of POP and Alum is known as Keene's cement. It is used chiefly as a gauging plaster in lime mortar for walls (as of hospitals, stores, railroad etc) where an unusually tough and durable plaster is required.
- **Uses:**
    - POP can be used for 3D printing. The water is applied by the inkjet head.
    - POP is used to produce fine artwork to decorate and beautify monuments and buildings. It is also used to imitate wood or stone which is found in ancient buildings.
    - It is used to heal broken bones and cast into a supportive coating known as an Orthopaedic cast.
    - Used in fireproofing and fire protection system.
    - Used to fill small gaps on walls & roofs.

4.6 GYPSUM:

Gypsum is the most common minerals of all the sulphate minerals. Gypsum is composed of hydrated calcium sulphate, and its chemical formula is $CaSO_4.2H_2O$. It is naturally occurring mineral, that appears soft white or grey in colour. It is formed in layered sedimentary deposits and has existed for millions of years since we can find it being used in Egyptian pyramids as well.

- **Preparation:** Although gypsum beds were formed naturally due to the evaporation of water from the massive prehistoric sea basins, it can also be synthesized. Synthetic gypsum is mainly obtained from coal-fired power plants, as a by–product of flue gas desulfurization.

  It can also be prepared by the action of dilute sulphuric acid on calcium carbonate or calcium chloride:

  $CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$

  $CaCl_2 + H_2SO_4 \rightarrow CaSO_4 + 2HCl$
- **Properties:**
    - Solid with a white crystalline structure that contains water molecules within itself.
    - It is a relatively soft mineral on the Mohs scale.
    - It is moderately soluble in water, and it can slowly dissolve in contact with moisture overtime.

- Its solubility decreases with increase in temperature.
- It has ability to undergo controlled dehydration when heated:

(i) When gypsum is partially dehydrated at 120^{0}C, it forms POP or calcined gypsum or gypsum plaster.

$2[CaSO_4.2H_2O] \overset{\Delta}{\rightarrow} 2CaSO_4.H_2O + 3H_2O$

(ii) When gypsum is heated to higher temperature, it produces Dead burnt plaster (anhydrous calcium sulphate) and quick lime.

$2CaSO4.H_2O \overset{\Delta}{\rightarrow} 2CaSO_4$ (Dead Plaster) + H_2O

$2CaSO_4 \xrightarrow{Heated} 2CaO$ (quick lime) + $2SO_2 + O_2$

- **Uses:**

- **Construction:**

  Drywalls (gypsum board), Plaster, Mouldings, floor underlayment, Fire resistant construction.

- **Agriculture:**

  Soil conditioner, source of nutrient (fertilizer).

- **Industrial:**

  Cement production (to regulate the setting time), paper & textiles, POP, and sulfuric acid manufacturing.

- **Art & Sculpture:**

  Intricate sculptures, statues, and bas-reliefs.

- **Medical:**

  Dentistry, Orthopaedic cast & splints.

Different Forms:

- Rock in dull colour.
- Alabaster – Fine grained variety.
- Selenite and Satin Spar – Fibrous texture with a silky lustre.

Questions

1. Which is the formula of dead burnt plaster? [MPPSC SFS Main 2020]
   - (a) Anhydrous magnesium sulphate
   - (b) Anhydrous calcium sulphate
   - (c) Hydrated calcium sulphate
   - (d) Hydrated magnesium sulphate
2. Chlorine is used as a bleaching agent. This bleaching property is due to [MPPSC SFS Main 2020]
   - (a) Reduction
   - (b) Chlorination
   - (c) Oxidation
   - (d) hydrogenation
3. Chemical formula of plaster of Paris is [MPPSC SFS Main 2021]
   - (a) $CaSO_4. 2H_2O$
   - (b) $CaSO_4. H_20$
   - (c) $CaSO_4. 1/2H_2O$
   - (d) $CaSO_4$
4. Oxidation state of chlorine in bleaching powder is [CGPSC ACF 2017]
   - (a) +1
   - (b) -1
   - (c) Zero
   - (d) +1 and -1
5. Temporary hardness of water is due to presence of which of the following? [Raj ACF 2018]
   - (a) $CaSO_4$
   - (b) $Ca(HCO_3)_2$
   - (c) $CaCl_2$
   - (d) $MgCl_2$
6. Aqueous solution of sodium carbonate is alkaline in nature because sodium carbonate undergoes: [CG labour inspector 2015]
   - (a) electrolysis
   - (b) Decomposition
   - (c) Ionization
   - (d) Hydrolysis
7. Among the following statements, the incorrect statement is [CG pariyojna 2021]
   - (a) The setting of plaster of Paris may be catalysed by sodium chloride
   - (b) During setting, the plaster of Paris converts into monoclinic form
   - (c) The setting of plaster of Paris is retarded by addition of borax
   - (d) Addition of alum to plaster makes the setting very hard
8. Match List-I with List-II and select the correct answer using following codes: [CG Pariyojna 2021]

	List-I	List-II
(A)	Baking powder	1.Sulphate and chlorides of calcium and magnesium
(B)	Permanent hardness	2. Available chlorine
(C)	Bleaching powder	3.Sodium-bicarbonate + Rochelle salt
(D)	Clinker	4.Mixture of silicates and aluminates
(E)	Red glass	5. copper oxide

Codes:

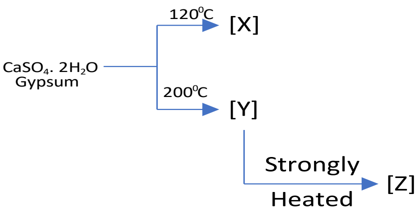
	(A)	(B)	(C)	(D)	(E)
(a)	3	1	2	4	5
(b)	1	2	3	4	5
(c)	4	3	1	2	5
(d)	1	3	4	5	2

9. Gypsum is added to clinker during cement manufacture to [CG Vyapam RFO 2021]
   - (a) Decreasing the rate of setting of cement
   - (b) Make the cement impervious
   - (c) Binding the particle of calcium silicate
   - (d) To facilitate the formation of colloidal gel
10. Consider following statements with references to sodium bicarbonate [CG Vyapam RFO 2021]
    - (A) Sodium bicarbonate is an intermediate product in Solvay ammonia soda process.
    - (B) Sodium bicarbonate is highly soluble in water.

(C) The solution of sodium bicarbonate is acidic in nature due to hydrogen atom.
(D) It gives pink colour with phenolphthalein.
(E) Baking powder is a mixture of Rochelle salt and sodium bicarbonate.

Wrong statements are
(a) A, B and C
(b) B, C and D
(c) A, B, and e
(d) C, D and E

11. [CG Vyapam RFO 2021]



[X], [Y] and [Z] are respectively

Codes

	[X]	[Y]	[Z]
(a)	Plaster of paris	Dead plaster	Calcium sulphide
(b)	Dead plaster	Plaster of paris	Calcium sulphite
(c)	Plaster of paris	Dead plaster	Lime
(d)	Anhydrous calcium sulphate	Plaster of paris	Calcium carbonate

12. Ion responsible for loss of bleaching action of bleaching powder due to its storage for long time is: [CGPSC ACF 2020]
(a) Cl^{-1}
(b) OCl^-
(c) ClO_3^- [given by CGPSC]
(d) ClO^-

13. Match List-I with List-II and select the correct answer using the codes given below lists: [CGPSC ACF 2020]

	List -I	List-II
(a)	Heavy water	1.biarbonates of Mg and Ca in water
(b)	Temporary hard water	2.No foreign ions in water
(c)	Soft water	3.D_2O
(d)	Permanent hard water	4. sulphates and chlorides of Mg and Ca in water

Codes:

	(A)	(B)	(C)	(D)
(a)	3	4	2	1
(b)	2	1	3	4
(c)	2	4	3	1
(d)	3	1	2	4

14. High boiling point of water is due to: [MH Forest service Main 2016]
(a) Weak dissociation of water molecules
(b) High disassociation of water molecules
(c) Hydrogen bonding among water molecules
(d) Van der Waals forces of attraction amongst the molecules

15. Sodium carbonate is used for the following purposes: [MH Forest service Main 2017]
(A) In the manufacture of glass and caustic soda.
(B) In softening of water.
(C) As a baking powder.
(D) In laundry as a washing soda.

Which of the statements given above are correct?

(a) A, B, C and D
(b) A, B and C only
(c) B, C and D only
(d) A, B and D only

16. Bleaching powder consist of [MHPSC forest Main 2021]
(a) Calcium Carbonate
(b) Calcium Hypochlorite
(c) Calcium Sulphate
(d) Magnesium Carbonate

17. Plaster of Paris consist of the following: [MHPSC forest Main 2021]

(a) Calcium sulphate
(b) Magnesium Sulphate
(c) Calcium Carbonate
(d) Magnesium Carbonate

18. Chemical formula of Bleaching powder is: [MPPSC SFM 2018]
(a) $CaOCl_2$
(b) CaOCl
(c) $CaClO_2$
(d) $CaOCL_3$

19. Which of the following is amphoteric in nature? [MPPSC SFM 2018]
(a) H_2O
(b) HCl
(c) NaOH
(d) HNO_3

20. On passing CO_2 through ab aqueous solution of Na_2CO_3, the compound formed is [MPPSC SFM 2018]
(a) NaOH
(b) H_2O_2
(c) $NaHCO_3$
(d) Na_2O

21. The molecular formula of Plaster of Paris is? [MPPSC SFM SP 2019]
(a) $2CaSO_4.\ 2HO(s)$
(b) $2CaSO_4.\ \frac{1}{2}H_2O(s)$
(c) $2CaSO_4.2HO(l)$
(d) $3CaSO_4.\ \frac{1}{3}H_2O(s)$

22. When carbon dioxide is bubbled through a brine solution, saturated with ammonia, which compound is formed? [MPPSC SFS Main 2020]
(a) $CaCO_3$
(b) Na_2CO_3
(c) $(NH_4)_2CO_3$
(d) $NaHCO_3$

Answer Key

1. b	2. c	3. c	4. d	5. b	6. d	7. b	8. a	9. a	10. d	11. c	12. c
13. d	14. c	15. d	16. b	17. a	18. a	19. a	20. c	21. b	22. d		

PREPARATION OF BUILDING MATERIALS

4.7 LIME:

Lime or quicklime as it is sometimes called is essentially calcium oxide with the chemical formula, CaO. Pure calcium oxide is a white solid which melts at 2570°C. It is an alkaline, crystalline chemical compound that is widely used in industries and pharmaceutical companies for its physical & chemical properties.

Preparation: The process of preparing calcium oxide is called calcination or lime burning. In this process the heating is applied to liberate a molecule of carbon dioxide, leaving only quick lime as the product:

- This process starts by thermal decomposition of materials such as seashells or limestone (rich in calcium carbonate) at high temperature of about 900°C – 1100°C.
- The reaction is reversible and endothermic, and carbon dioxide immediately begins to form in the lime kiln. It leaves back the white caustic calcium oxide substance.

$CaCO_3 \overset{\Delta}{\Leftrightarrow} CaO + CO_2$

Note:

Here, this reaction will be irreversible, if happens in an open container and it will be reversible, if happens in a closed container.

Properties:

- White, amorphous, and odourless solid.
- It has a high melting point and due to that, used as refractory material.
- It is known to emit an intense glow, when it is heated to high temperature of about 2400°C. This form of illumination is known as limelight.
- It absorbs moisture on exposure to the atmosphere and the product formed is calcium hydroxide [$Ca(OH)_2$] also known as slaked lime. this process is known as slaking of lime.
  $CaO(S) + H_2O(l) \rightarrow Ca(OH)_2\ (aq)$
- After absorbing CO_2 From the atmosphere, it produces calcium carbonate:
  $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$

Uses:

- Used in manufacturing of cement, sodium carbonate, and dyestuff.
- Used in the purification of sugar.
- Medicinal purposes as well as for the development of insecticides and pesticides.

4.8 CEMENT:

Cement, one of the most important buildings materials, is a binding agent that sets and hardens to adhere to building units such as stones, bricks, tiles etc. The precursor to modern day cement was created in 1824 by Joseph Aspdin. Cement generally refers to a very fine powdery substance chiefly made up of limestones (calcium), Sand (silicon), bauxite (aluminium) and iron ore.

Chemical Composition: Cement or Portland cement is made up of four main compounds: Tricalcium silicate ($3CaO.SiO_2$) (30-50%), Dicalcium silicate ($2CaO.SiO_2$) (20-45%). tricalcium aluminate ($3CaO.Al_2O_3$) (8-12%) and tetra calcium aluminoferrite ($4CaO.Al_2O_3.Fe_2O_3$) (6-10%).

Ingredient	Percentage in cement
Calcium Oxide (CaO)	62%
Silica (SiO_2)	22%
Aluminium (Al_2O_3)	5 – 8%
Iron oxide (fe_2O_3)	2 – 3 %
Magnesia (MgO)	2 – 3%
Sulphur tri oxide (SO_3)	1 – 2%
Alkalis	1%

Preparation:

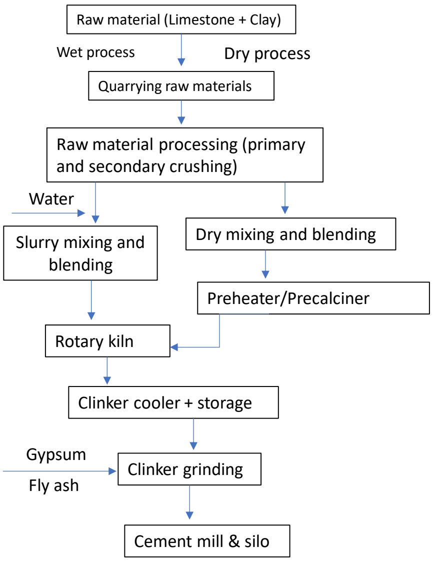
The manufacturing of cement generally involves four steps:

(i) Mixing

(ii) Burning

(iii) Grinding

(iv) Storage



1. **Mixing:**

   Mixing of raw materials can be done either with dry or wet process. In dry process the calcareous and argillaceous materials are grinded to the required size and then they are mixed and ready to be fed in rotary kiln. In wet process both materials are grinded and then argillaceous materials are washed with water. Then both the materials are mixed to make a paste (slurry).

2. **Burning:**

   This process is carried out in rotary kiln, A large unit that rotates slowly on an axis that is inclined a few degrees. This Kiln is lined with refractory bricks, so that it can withstand higher temperature (about 1500^0 – 1700^0C). The material introduced at the upper end, moves down slowly to the lower or firing end. Both the materials react to form calcium silicates and calcium aluminates and these aluminates & silicates fuse together form small and hard stones known as clinkers.

3. **Grinding:**

   The clinkers obtained from rotary Kiln are very hot hence they are first cooled by air and then fed to grinders in-order to reduce their size. The clinkers are then feed into ball mill along with powdered gypsum. The gypsum acts as a retarding agent, so that the resulting cement does not set quickly, when it comes in-contact with water.

4. **Storage:**

   The grinded cement is then stored in silos, then shipped and marketed.

- **Reactions in rotary Kiln:**

$CaCO_3 \xrightarrow{850^0C} CaO + CO_2$ $[oxides]$

$MgCO_3 \xrightarrow{650^0C} MgO + CO_2$ $[oxides]$

$CaO + SiO_2 \xrightarrow{900^0C} CaO.SiO_2$ (calcium silicate)

$CaO + Al_2O_3 \xrightarrow{900^0C} CaO.\ Al_2O_3$ (Calcium aluminate)

Now making of alite, belite & Celite happens:

$Cao.SiO_2 + CaO \xrightarrow{1300^0C} 2CaO.SiO_2/C_2S$ (Dicalcium silicate /belite)

$CaO.Al_2O_3 + 2CaO \xrightarrow{1300^0C} 3CaO.Al_2O_3/C_3A$ (tricalcium aluminate/celite)

$3CaO + SiO_2 \rightarrow 3CaO.SiO_2\ /C_3S$ (Tricalcium silicate /Alite)

$4CaO + Al_2O_3 + Fe_2O_3 \rightarrow 4CaO.Al_2O_3.Fe_2O_3/C_4AF$ (Tetra calcium Alumino ferrite/ felite)

Note:

- Gypsum is added in the cement manufacturing to slow down the setting of cement.
- Excess of calcium carbonate resulting in shrinkage cracks, since calcium carbonate occupies lesser volume than calcium hydroxide.
- Excess of Alumina reduces the strength of the cement and increases the quick setting property as well.
- Excess of silica increases the strength of the cement and its setting time become prolonged as well.

Properties:

- Cement undergoes a chemical reaction called hydration when mixed with water, leading to the setting, and hardening of the material (concrete). The setting time can be manipulated by adjusting the composition of the cement.
- Cement provides compressive strength to the concrete structures it forms. The strength of cement depends on factors like curing conditions, water-cement ratio, and the type of cement used.
- The fineness of cement particles affects its hydration rate and, consequently, the setting and hardening process.
- The heat released during the hydration process can affect the temperature of large concrete structures.

Uses:

- The most common use of cement is in the production of concrete, which is a composite material used in construction for various applications like buildings, bridges, roads, and more.
- Cement is an essential component of mortar, which is used to bind bricks or stones in construction.
- Cement is used to stabilize soil, and enhancing its load-bearing capacity.

- Cement is used to manufacture precast concrete products such as pipes, blocks, panels, and other structural elements.
- Cement-based grouts are used for filling voids, cracks, and gaps in structures.
- A specialized type of cement is used in oil wells to ensure the integrity of wellbore and prevent fluid migration.
- Asbestos cement, which includes cement mixed with asbestos Fibers, was historically used for roofing, pipes, and other products (note: asbestos usage is now limited due to health concerns).
- Coloured and special cements are used for decorative purposes in flooring and other architectural features.

Types:

- **Ordinary Portland cement:** ordinary Portland cement is the most widely used type of cement manufactured and used worldwide. "Portland" is a generic name derived from a type of building stone quarried on the Isle of Portland in Dorset, England. OPC is suitable for most general concrete jobs and mortar or stucco construction projects.
- **Portland pozzolana cement:** Manufacturers create Portland pozzolana cement by grinding pozzolanic clinker (fly ash, silica fume, or volcanic ash), sometimes with additives of gypsum or calcium sulphate, with ordinary Portland cement. Compared to OPC, it has a higher resistance to various chemical reactions within concrete. PPC is often used for projects like bridges, piers, dams, marine structures, sewage works or underwater concrete projects.
- **Rapid hardening cement:** it has high strength in the early stages of the hardening process. Its strength in three days is comparable to OPC strength at seven days with the same water-to-cement ratio. Rapid-hardening cement may have an increased lime content, combined with a finer grinding process, or better strength development. It is often used for projects with early-stage formwork removal or when the focus is on increasing construction rates and decreasing cost.
- **Quick setting cement:** Similar-to extra-rapid-hardening cement, this concrete type may set and become stronger even quicker than OPC and rapid-hardening cement. Its grain and strength rate are similar-to OPC, but it hardens faster. Quick-setting cement may be beneficial for time-sensitive projects or those located near stagnant or running water.
- **Waterproof cement:** It is also called hydrophobic cement. The process of manufacture of this special cement is same as that of Portland cement. The clinkers formed in the manufacture of cement are grinded with water repellent film substance such as Oleic (Tanic) Acid or Stearic Acid. These chemicals form a layer on the cement particle and does not allow water to mix and start hydration process in the transportation or storage stage. It is used in longer storage periods and extremely wet climatic conditions, like in the Tunnel construction as the underground repairs are difficult and costly.
- **White cement:** White cement is similar-to OPC but has a white colour due to the absence of iron and manganese oxides. Used for architectural purposes and for making coloured concrete and interior and exterior decorative projects like designing garden paths, floors, swimming pools and ornamental concrete products.

4.9 GLASS:

Si-OH + Si-OH → Si-O-Si + H_2O (glass network formation)

Si-OH + Si-OR → Si-O-Si +ROH (gelation)

Si-OR + H_2O → Si-OH + ROH (hydrolysis)

Glass is an inorganic solid and non- crystalline material that is transparent in appearance. It is an amorphous solid substance, though glass is not considered as true solid, as it is a frozen liquid. It resembles a solid due to the great increase in its viscosity when it is cooled rapidly. Thus, glass is a super cooled liquid which chemically composed of metal silicates & Silica, with the chemical formula Na_2SiO_3. $CaSiO_3$. $4SiO_2$.

Glass has a bonding of Si-O.

- **Manufacturing of glass:** It majorly involves 3 steps:
  (i) **Fusion of Raw material:** Soda ash (Na_2CO_3), Lime stone ($CaCO_3$) and sand (SiO_2) are mixed proportionally and finely ground. This powder mixture is called as batch. Some cullet (broken glass) is mixed with the batch to lower the melting point of raw material. This mixture is heated at $1000^0C – 1400^0C$ in a furnace and the fusion results in liquid glass.

  The chemical reaction involved are:

  $Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$

  $CaCO_3 + SiO_2 \rightarrow Ca_2SiO_3 + CO_2$

  After these, the sodium silicate & calcium silicates formed above, mixes with silica to form glass. The glass formed here is in molten state, so it can be given any shape by cooling it in the moulds of desired shape & size.

  (ii) **Working with molten mass:** The fused molten glass is said to cool for certain level, still it is in liquid state. The Partially cooled down glass is poured in moulds of required shape.

  (iii) **Annealing of glass:** The last stage of glass manufacturing is annealing, in which the glass is strengthened. If glass is allowed to cool rapidly, it becomes very brittle, thus it is cooled gradually by passing it through various temperature zones from high to low temperature over conveyor belts. The result is solid transparent glass.

  Various types of glasses can be obtained by varying the proportions of the raw material in a batch, or by treating the batch with different chemicals to get the desired properties.

- **Types of glass:**
  - **Soda Glass:** It is easily fusible, so it is use for window panes and to manufacturing bottles, jars, and mirrors. It is also called as soft glass.
  - **Pyrex Glass:** It can withstand very high temperatures and it has a low coefficient of expansion hence is used for kitchenware, laboratory glassware, chemical apparatus (thermometers) and ovenware.
  - **Quartz Glass:** Quartz glass is used to make electrical bulbs, optical devices, and refractory materials.
  - **Potash Glass:** It can withstand higher temperatures and is more resistant to the action of acids. Hence it is used in hard glass laboratory tools.
  - **Coloured Glass:** It is obtained by adding metal oxides or metal salts before it is annealed. It is used to make jewels, gems. Lead crystal glass is used to make decorative items.

- **Flint Glass:** the components of flint glass are silica, lead oxide and potassium carbonate. It is used in optics, lenses, prisms, and nuclear installations. It is also known as lead glass or optical glass. Flint glass is not affected by acids; is highly transparent; has a high refractive index and absorbs radiations.
- **Photo - chromatic Glass:** Some sunglasses or goggles have photo-chromatic glass. The silver bromide in the glass reduces the intensity of bright light before it reaches our eyes and keeps out the U-V radiations.
- **Bullet-Proof Glass:** Safety glass or bullet–proof glass, such as those used in aeroplanes and high - security cars, is made by pressing and binding two glass sheets with a thin thermoplastic sheet in between. This is also called laminated glass. When this glass breaks; It does not leave any sharp edges. Means it is splinter-proof. Poly carbonates are used as thermoplastic in this.
- **Crooks glass:** It mainly comprises of silica and cerium oxide (CeO_2) which absorbs the ultraviolet radiations from the sun. this is why crooks glass is used in sunglasses.
- **Fibre Glass:** It is used in industrial insulation, and in furniture articles such as tempered glass tops. It is made up of sand, Soda ash and lime stone. Fibre glass is manufactured by passing the molten mass through minute holes in metallic cylinders, making it as strong as steel. It is used to make refrigerators and electric furnaces, as it is heat-resistant.

Material that adds colour in Glass:

Cobalt Oxide	Deep blue
Selenium Compounds	Red
Carbon Oxides	Amber/ Brown
Copper Compounds	Red/ Green
Lead with Antimony	Yellow
Iron Oxide	Green/ Brown
Antimony Oxide	White
Calcium Sulphide	Yellow
Chromium Oxide	Green
Manganese Di oxide	Purple

4.10 STEEL:

Iron in the pure form is shock proof, ductile but it is less durable. When small amount of carbon is added to pure iron, it increases the strength of the iron, which is called as steel. This steel is an alloy of iron and carbon, which contains 98% of iron and 2% of carbon.

Manufacturing of steel: Steel is manufactured in industries by using three methods.

1. **Cementation Process:** Cementation is an obsolete method to manufacture steel. In this process wrought iron was heated in sealed pots in a coal fired furnace. The furnace is heated at 1000^{0}C for 8 – 10 days. The coal burns to form carbon monoxide which is absorbed in the iron rods and further decomposed to form carbon and carbon dioxide. As the amount of carbon increased, it changed these wrought iron rods into steel. The released carbon dioxide caused blisters on the surface of the steel and therefore the steel produced by this method is called blister steel.
2. **Bessemer's Process:** The Bessemer process was the first inexpensive industrial process, that allowed for mass production of steel. Before the development of an open mouth furnace, the process used a molten pig iron to melt iron. The real difference with this process is that air was forced through the molten iron to remove impurities.

The Bessemer process can be broadly categorized into two types: Acid Bessemer process and Basic Bessemer process. The primary difference between the two lies in the type of lining used in the converter, which affects the composition of the final steel product.

Acid Bessemer process: The iron used in this process must not contain phosphorus and sulphur.

- **Converter Living:** This process uses a converter lined with acidic refractory material, typically made of silica (silicon dioxide). The acidic lining reacts with the basic impurities present in the pig iron.
- **Charging the converter:** Molten pig iron is charged into the acidic Bessemer converter.
- **Blowing Air:** Air is blown through the molten pig iron, oxidizing the impurities, particularly carbon and turning them into oxides. The chemical reactions raise the temperature of the molten metal. The impure carbon is oxidised to form carbon mono oxide, which burns at the top with blue flame.

  $Si + O_2 \rightarrow SiO_2$

  $2Mn + O_2 \rightarrow 2MnO$
- **Formation of Acidic slag:** Both the oxides react to form a silica–rich acidic slag, which floats on the surface of the molten metal.

  $MnO + SiO_2 \rightarrow MnSiO_3$ (slag)
- **Tapping the steel:** After adding spiegel (an alloy of C,Fe & Mn) to the iron, once the desired steel composition is achieved, the converter is titled and the steel is taped into ladles. Here the slag and steel are separated.

Basic Bessemer Process: Basic process is adopted if sulphur and phosphorus is present as an impurity.

(i) **Converter lining:** This process uses a converter lined with basic refractory materials, such as magnesite ($MgCO_3$) or dolomite [$CaMg(Co_3)_2$]. The basic lining reacts with acidic impurities present in the pig iron.

(ii) **Charging the converter:** Molten pig iron is charged into the basic Bessemer converter.

(iii) **Blowing Air:** Air is blown through the molten pig iron oxidising the impurities, and turning them into oxides.

$4P + 5O_2 \rightarrow 2P_2O_5$ (Phosphorus Pentoxide)

(iv) **Formation of basic slag:** The basic lining reacts with the acidic impurities to form a basic slag, rich in oxides of calcium and magnesium. This slag floats on the surface of the molten metals.

$3CaO + P_2O_5 \rightarrow Ca_3(PO_4)_2$ (slag)

(v) **Tapping the steel:** Once the desired steel composition is achieved, slag and steel are separated. One of the significant advantages of the Bessemer process was its speed, efficiency, and inexpensive nature. However, it had limitations, which led to the development of open-hearth process.

3. **Semen-Martin's open-hearth process:** The process was invented by Pierre Martin in 1864. Earlier carl siemens made significant advancements in the design and operation. The open-hearth furnace comprises a shallow hearth with a low roof and is line internally by either silica or lime. Raw materials of this process are – cast iron, scarp iron and hematite (Fe_2O_3). The impurities of sulphur, silicon and manganese are oxidised by hematite. The percentage of carbon is decreased by adding scrap iron. The heat required for the process is obtained by burning heated producer gas ($CO+H_2$). Depending upon impurities the lining of the hearth is either acidic or basic. At last, the percentage of carbon maintained by adding the required amount of Spiegel (An alloy of C, Fe & Mn).

The reactions during this process are:

$3C + 2Fe_2O_3 \rightarrow 4Fe + 3CO_2$

$3S + 2Fe_2O_3 \rightarrow 4Fe + 3SO_2$

$3Si + 2Fe_2O_3 \rightarrow 4Fe + 3SiO_2$

If phosphorus is present:

$6P + 5Fe_2O_3 \rightarrow 10Fe + 3P_2O_5$

$P_2O_5 + 3CaO \rightarrow Ca_3(PO_4)_2$ (Slag)

Like Bessemer process, calcium silicate and calcium phosphate are obtained as a slag in this process. After testing the quality additional materials such as ferromanganese or other alloys could be added to achieve the desired steel composition.

Types: Steel changes its mechanical properties based on the chemical composition or alloying element. It can be divided into 4 types – (a) carbon steel, (b) alloy steel, (c) stainless steel, (d) tool steel.

(i) **Carbon steel:** Steel with a carbon content of between 0.05 wt % and 2.1 wt % is known as carbon steel. These are the most used type in the manufacturing industries.

(ii) **Stainless steel:** Stainless steel is a steel alloy containing 10.5% chromium. With a thin coating of Cr_2O_3 on its surface, stainless steel shows corrosion-resistant qualities. There are various types of stainless steel: Ferritic, Martensitic, Austenitic, Duplex, and Precipitation-Hardening (PH) Stainless Steels.

(iii) **Tool steel:** Tool steels contain between 0.5 wt % and 1.5 wt % carbon. Increased carbon content increases hardness and strength. Typically, these steels are used to manufacture tools and die. There are not many types of tool steel but one prominent is High-Speed Steel (HSS), which is mostly used in the manufacturing of cutting tools for machines.

(iv) **Alloy steel:** Carbon steel is combined with one or more alloying elements, such as manganese, silicon, nickel, titanium, copper, chromium, and aluminium, to produce alloy steel.

Types of alloying elements	Significance in the alloy
Manganese (Mn)	It is renowned for its exceptional hardening properties and wear resistance. The higher manganese content increases the strength of the alloy steel while simultaneously increasing the carbon equivalent value.
Silicon (Si)	Silicon steel is the most crucial material in terms of magnetic force. With 1-2% silicon addition, steel is primarily used to produce permanent magnets.
Nickel (Ni)	This is the most popular alloy steel in the world. It is composed of 3.5% nickel and 0.35 % carbon. Nickel Steel is renowned for its structural steel-like strength without its ductility. The addition of nickel increases the material's toughness, making it more resistant to damage caused by high-impact loads and shocks.
Chromium (Cr)	The addition of Cr increases the hardenability of alloy steel along with corrosion resistance.
Tungsten (W)	The primary component of tungsten steel, also known as wolfram, is silver metal, which has the highest melting point of all known metals. It is corrosion- and wear-resistant and can withstand high temperatures.
Vanadium (V)	This steel is well-known for its corrosion resistance and shock absorption capabilities. It is used in chemical-carrying pipes and tubes, as well as as a fine layer to bond titanium to steel for aerospace and automobile applications.
Sulphur (S)	Sulphur content must be kept to a minimum. When it is added in higher concentrations, the alloy steel becomes brittle when rolled and twisted.
Copper (C)	The mechanical properties of the pearlitic microstructure are stabilised by copper, enhancing its corrosion resistance.
Titanium (Ti)	Corrosion resistance and overall strength is improved by the addition of Titanium.

Questions:

1. Waterproof cement contains [MPPSC SFS Main 2021]
   - (a) Calcium stearate
   - (b) Aluminum stearate
   - (c) Tannic acid
   - (d) All of the above
2. Portland cement does not contain [CGPSC ACF 2017]
   - (a) Ca_2SiO_4
   - (b) $CaSiO_3$
   - (c) $Ca_3Al_2O_6$
   - (d) $Ca_3(PO_4)_2$
   - (e) None of these
3. Which of the following is an amorphous solid? [CGPSC ACF 2017]
   - (a) Sugar
   - (b) Sodium chloride
   - (c) Diamond
   - (d) Glass
   - (e) None of these
4. Match List -I with List-II and select the correct answer using codes given below: [CG labour inspector 2015]

List -I	List -II
(A) Cement	1. Sodium salt of higher fatty acids
(B) Glass	2. Carbon black
(C) Ink	3. Sodium oxide, calcium oxide and silica
(D) Soap	4. Aluminates and silicates of calcium

Codes:

	(A)	(B)	(C)	(D)
(a)	4	3	2	1
(b)	1	3	2	4
(c)	1	2	3	4
(d)	4	2	3	1

5. The glassware used in kitchen are made of Pyrex glass because it has______ coefficient of expansion. [CG labour inspector 2015]
   - (a) High
   - (b) Low
   - (c) Medum
   - (d) None of the above
6. Consider the following statements: [CG Pariyojna 2021]
   - (A) Selenium impacts red colour in glass
   - (B) Boron trioxide increase coefficient of expansion of glass.
   - (C) Flint glass is higher suitable for making laboratory glass-wares.
   - (D) Crooke's glass does not allow passage of ultraviolet rays.
   - (E) Pet furnace method is use to prepare large quantity of glass.

   Incorrect statements are:
   - (a) 1,2 and 3
   - (b) 2,3 and 5
   - (c) 1,4 and 5
   - (d) 3,4 and 5
7. The chemical composition of ordinary glass can be written as follows: [MPPSC SFM 2018]
   - (a) $Na_2SiO_3.CaSiO_3.\ 4SiO_2$
   - (b) $Na_2SiO_3.\ CaSiO_3.\ 6SiO_2$
   - (c) $Na_2O.CaO.\ 4SiO_2$
   - (d) $Na_2SiO_3.CaSiO_3.\ 2SiO_2$
8. Glass has bonds of? [MPPSC SFM SP 2019]
   - (a) C—O
   - (b) Si – O
   - (c) Ge – O
   - (d) Sn – O
9. Concrete gains strength due to? [MPPSC SFM SP 2019]
   - (a) Chemical reaction of cement with sand and coarse aggregates

(b) Evaporation of water from concrete

(c) Hydration of cement

(d) All of the above

10. Which one has the highest percentage in Portland cement? [MPPSC SFS Main 2019]

(a) Fe_2O_3

(b) CaO

(c) SiO_2

(d) Al_2O_3

Answer Key

1. d	2. d	3. d	4. a	5. b	6. b	7. a	8. b	9. c	10. b		

CHAPTER

5

METALS AND THEIR GENERAL PROPERTIES

Syllabus: Metals: introduction, position of metals in periodic table; Non-metals, position of non-metals in periodic table; Ores & Alloys

5.1 INTRODUCTION:

Metal, any of a class of substances characterized by high electrical and thermal conductivity, as well as by malleability, high reflectivity of light and ductility. Metals are the elements which have free electrons, so they form +ve ions (Cations) by donating electrons, means they are electro-positive.

For ex: Sodium, Copper etc.

$M \rightarrow M^{+n} + ne^-$

(metal) (cation) (Electron)

- **Physical properties:**
  - **Malleability**: Metals are malleable, *i.e.*, metals can be beaten into thin sheets without breaking it. Exceptions- Zinc, mercury and Antimony are non-malleable.
  - **Ductility:** Metals are ductile *i.e.* metals can be drawn into wires.
    Exceptions- zinc, mercury and Antimony are non-ductile.
  - **Lustre:** They are lustrous or shiny and can be polished. (Except Sodium).
  - **Conductivity:** They are good conductor of heat and electricity.
    Exceptions:
    Heat: Lead, mercury, Titanium, Aluminium.
    Electricity: Mercury, Tungsten, Titanium, Aluminium.
  - **Hardness:** They are generally hard and strong. (Except Sodium & Potassium).
  - **Density:** Metals have high density, except Lithium, Sodium and Potassium.
  - **Melting and Boiling points:** They have high melting and boiling points, (except sodium potassium, mercury, and cesium).
  - They are solid at room temperature. (Except Mercury, which exists in liquid state at room temperature).
- **Chemical Properties:**
  - **Reaction with Oxygen:** When metals are burnt in air; They react with the Oxygen to form metals oxide:
    $4\,Na(S) + O_2(g) \rightarrow 2Na_2O(s)$ (Sodium Oxide)
    $2Mg + O_2 \rightarrow 2MgO$

$4Al + 3O_2 \rightarrow 2Al_2O_3$

Note: The aluminium oxide shows acidic as well as basic properties, and known as **Amphoteric oxide**. Zinc also forms same oxide. Amphoteric oxides react with acid and base to form salt and water. Some other examples of metals that form amphoteric oxides are lead, tin, iron, chromium, gallium, beryllium etc.

$Al_2O_3 + 6HCl \rightarrow 2 AlCl_3$ (salt) + $3H_2O$ (Water)

$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$

- **Reaction with water:** When metals react with water (cold or hot), the product formed are metal hydroxide and with steam it gives metals oxide.

  $2K(s) + 2H_2O \xrightarrow{Exothermic} 2KOH + H_2$ [Cold water]

  $Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$ [Hot water]

Note: The reaction with cold water will be exothermic and with hot water, it will be a normal one.

$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$

(steam) [Aluminium oxide]

- **Reaction with acid:** Metals usually displace hydrogen from dilute acids. Only less reactive metals like copper, silver and gold do not displace it. **For ex:**

  $2Na + 2HCl$ (Acid) $\rightarrow 2NaCl$ (metal salt) + H_2

- **Reaction with salt solutions:** When a more reactive metal is put in the salt solution of less reactive metal, then the more reactive metal displaces the less reactive metal from its salt solution. **For ex:**

  $CuSO_4 + Zn \rightarrow ZnSO_4 + Cu$

  (blue sol.) (Colourless sol.)

- **Reaction with chlorine:** After reacting with chlorine metals form metal chlorides.

  $2Na + Cl_2 \rightarrow 2NaCl$

- **Reaction with hydrogen:** Most of the metals do not combine with hydrogen. Only a few like Sodium, potassium, calcium, and magnesium reacts with hydrogen to form hydrides.

  $2Na + H_2 \rightarrow 2NaH$

Note: Aqua Regia- A freshly prepared mixture of one part of concentrated nitric acid and three parts of concentrated hydrochloric acid. It is a highly corrosive and fuming liquid, which can dissolve all the metals even gold and platinum too.

5.2 POSITION OF METALS IN PERIODIC TABLE:

Approximately three-quarters of all known chemical elements in periodic table are metals. The periodic table was first created by Mendeleev and after that Moseley presented a revised form in 1913, which is known as 'The modern Periodic Table'. The periodic Table is based upon the periodic law, which states that-''The physical and chemical properties of the elements are periodic functions of their atomic numbers.''

The metals are categorized into S, P, D and F blocks:

1. **S - Block:** The elements in which the last electron enters the outermost s-orbital are called S-block elements. Alkali and Alkaline Earth metals represents the S-block of periodic table and their compounds find wide application in our daily life and industries as well.

   Here 2 Major Groups are present in S-block:

   Group 1: Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Cesium (Cs), Francium (Fr)

These metals are called Alkali metals. Hydrogen is exception to this group as it is not a metal.

Properties:

- Atomic and ionic radii increase while going down from Li to Cs.
- Ionization energy and electron affinity decreases going down in group and density increases. [Exception K < Na]
- **Flame colouration:** Li – crimson red, Na – yellow, K- violet, Rb- Red violet, Cs – blue.
- Low melting and boiling points. (Cs has lowest M.P. of about 28.5)
- All, form MX type halides with halogens. (where X = F, cl, Br, I).

Group 2: Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba), Radium (Ra)

These metals are called the alkaline earth metals. Be, Sr and Ba are rare, Ra is instable and highly radio-active. In contrast Ca and Mg are found in abundance on earth.

Properties:

- The atomic and ionic radii of alkaline earth metals are smaller than those of the corresponding alkali metals and increases while going Be to Ra.
- Density decreases from Be to Ca and increases from Ca to Ra.
- **Flame colourization –** Ca – Brick Red, Sr – crimson, Ba – apple green, Ra – Crimson.
- They have low melting and boiling points, but are higher than the corresponding alkali metals due to smaller size.
- All, Form MX_2 type halides with halogens.

Anomalous properties of some S-block elements:

- **Lithium:** The melting and boiling points of Lithium are higher than other alkali metals.
  - Unlike other alkali metals, lithium chloride crystallises to form a hydrate ($LiCl_2.H_2O$).
  - Lithium forms nitride while other alkali metals do not.
    $6Li + N_2 \rightarrow 2Li_3N$ (Lithium Nitride)
  - Compounds of lithium are partially soluble in water, whereas others are highly soluble in water.
  - Lithium nitrate decomposes to form an oxide whereas other metals on heating give nitrites.

  Lithium exhibits such unique properties due to the small size of lithium atom, high polarising power and hydration energy.

- **Beryllium and its diagonal relationship with Aluminium:**
  - The anomalous properties of beryllium are mainly due to its small size, high electro-negativity, high ionization energy and polarizing power:
  - The melting and boiling points are higher when compared to the other elements of the group.
  - They form covalent bonds, whereas the other members of the group-2 form ionic bond.
  - The hydroxides of both Beryllium and aluminium are amphoteric in nature, whereas other elements of group–2 are basic.
  - The two metals **do not** impart colour to the Bunsen flame.
  - Both Be and Al do not react with water like other elements of group -2.

- Beryllium is harder than other group members and does not react with water even at high temperature.

2. **P- Block:** The elements in which the last electron enters to the outermost p-orbital are called P-block elements. As the maximum number of electrons that can be accommodated in a set of P orbitals is six, therefore there are six groups of P-block in the periodic table. Metals, Metalloids (semi-metals) and Non-Metals all are present in this block:

- Elements are categorized from group 13 to 18 (III A to viii A).
- Group 16 (vi A) is called Chalcogen because most ores of copper (Green Chalkos) are oxides or sulphides and such ores contain traces of selenium and Tellurium.
- Group 17 (vii A) is called Halogens, Greek halo (Sea salt) and gens (producing or formation) means sea salt former.
- Group 18 (viii A) is called Nobel gases or Inert gases as their valence shell orbitals filled completely. Because of this; they react with a few elements only and that too under certain conditions.
- Group 13: This group is also called boron family. The elements are Boron (Non-metal), Aluminium, Gallium, indium, Thallium (metals). They each have three electrons in their outermost shell.

Properties:

- Atomic Radii: B > Ga < Al < In< Tl
- Ionization Enthalpy: B > Tl > Ga > Al > In
- Melting Points: B > Al > Tl > In > Ga
- Boiling Points: B > Al > Ga > In > Tl

Note: The inert pair effect- The tendency of the two electrons in the outermost atomic S-orbital to remain unshared in compounds of post – transition metals (Group -13,14,15,16) The outermost S electron pairs are more tightly bound to the nucleus in these atoms. The 5s electron of tin (Sn) and 6s of Lead (Pb) can be examples of this.

3. **D-block Elements:** The d block elements are found in groups 3 to 12 of the periodic table. D-block elements are also known as the transition metals because-

- They show variable oxidation state in their compounds.
- There outermost (nth) and penultimate (n-1) shell is incomplete.
- Their position in the periodic table is between S and P block. Hence their properties are transitional between highly reactive metallic elements of S block (ionic in nature) and P block (covalent in nature).

Note: Not all d block elements count as transition metals, because few elements like Scandium (Sc) and Zinc (Zn) do not have incompletely filled d orbitals. Scandium ion has no d electron and zinc ion has full d-orbitals hence they do not meet the definition. Apart from these, cadmium (Cd) and mercury (Hg) are not considered as transition elements.

Properties:

- All the transition metals are metals, thus possess all qualities of metals.
- Covalent and metallic both the bonding exists in the atom of these elements. The presence of unfilled d-sub shell favours covalent bonding and metallic bonding is due to possession of one or two electron in outermost energy shell.

- The transition elements have very high melting and boiling points as compared to those of S&P block elements.

4. **F- block:** The elements in which the additional electron enters in (n-2) f orbitals are called inner transition elements, or F-block elements. The elements belonging to f- block are further classified into:
    - Lanthanides: The first series (4F) of elements are called lanthanides and these elements have atomic numbers from 57 to 71. These elements are non–radioactive (except promethium). Lanthanides are reactive elements so are not found freely in nature. They have three outer shells incomplete. They are highly dense metals with high melting points (not in regular trend) and are good conductors of heat and electricity.

      Lanthanides (Z=58–71) (Ce-Lu)
    - Actinides: The second series of elements are called actinides and include elements with atomic numbers 89 to 103 (Th- Lr). An extra electron enters 5f orbitals of (n-2)th shell in these elements. Thorium (Th), Protactinium (Pa) and Uranium (U) are natural elements. They all are radioactive due to instability and have ability to undergo nuclear reaction.

      Actinides (z = 90 – 103) (Th – Lr)

Note:

- Elements with atomic number 103 is Lawrencium with the symbol Lr (Formerly Lw).
- If the formula of the nitride of a metal is MN, where M represents the metal, then the formula of its sulphate can be determined by considering the charges of the ions involved. The nitride ion is typically N^{3-}, meaning it carries a charge of -3. Since the metal M is not specified, Let's represent its charge as X.

  Now, for the nitride (N^{3-}) and metal (MX), the charges must balance to create a neutral compound. Therefore:

  $x + (-3) = 0$

  Solving for x, we find that $x = +3$.

  So, the metal M has a charge of +3.

  Now, for the sulphate ion ($SO4^{2-}$), we know that it carries a charge of -2.

  To balance the charges and create a neutral compound, we need two sulphate ions for every three metal ions. Therefore, the formula for the sulphate of the metal MN is $M_2(SO_4)_3$.

Questions

1. Alkaline earth metals are denser than alkali metals, because metallic bonding in alkaline earth metals is [CGPSC ACF 2020]
    (a) Stronger
    (b) Weaker
    (c) Volatile
    (d) Not present

4. Position of potassium in periodic table is [CGPSC ACF 2017]
    (a) Group -I, period -IV
    (b) Group -II, period -III
    (c) Group – III, period – IV
    (d) Group -I, period – II
    (e) None of these

5. “Metals are usually not found as nitrates in their ores: [CGPSC ACF 2020]

2. The formula of nitride of a metal is MN. The formula of its sulphate will be [CG pariyojna 2021]
   (a) MSO4
   (b) M_2SO_4
   (c) $M_2(SO_4)_3$
   (d) $M(SO_4)_2$
3. Elements of following group in the periodic table are called ‘chalcogens’ [CGPSC ACF 2017]
   (a) Group-18
   (b) Group-17
   (c) Group-16
   (d) Group-15
   (e) None of these

Out of the following two (I and II) reasons which is/are true for the above observations?

(A) Metal nitrates are highly unstable.

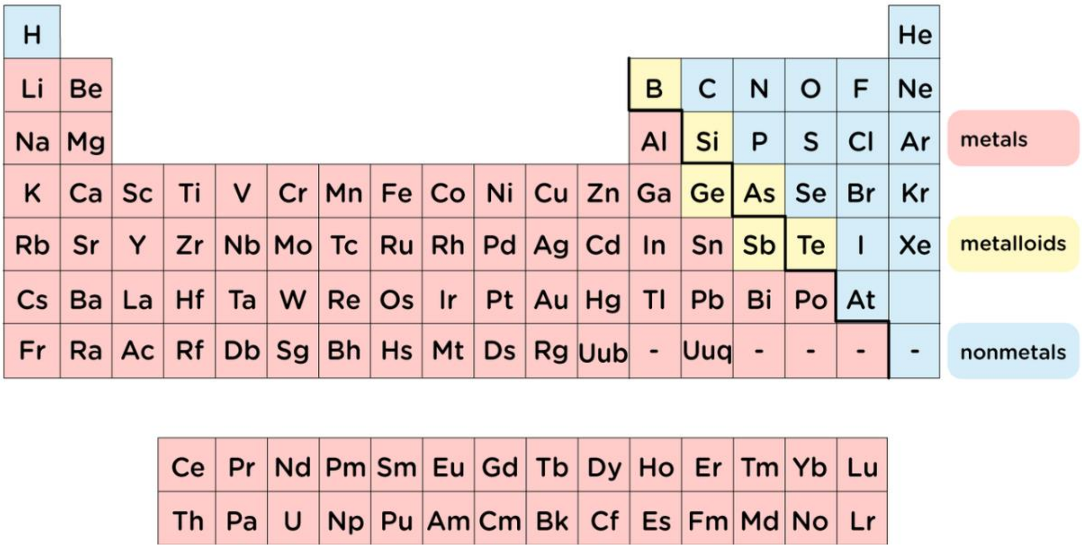
(B) Metal nitrates are highly soluble in water

Codes:

(a) A and B are false
(b) A is false, but B is true
(c) A is true, but B is false
(d) A and B are true

1. (a), 2. (c), 3. (c), 4. (a), 5. (b)

Metals, Nonmetals, and Metalloids



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	-	Uuq	-	-	-	-

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

5.3 NON-METALS:

Non-metals are the elements that are poor conductor of electricity and heat and are neither malleable nor ductile. Properties of nonmetals are usually the opposite of properties of metals-

- Out of all non-metals most are gases (like hydrogen, oxygen); one is liquid (bromine); and few are solid (like carbon, sulfur).

- Non-metals are elements which form negative ions(anions) by gaining electrons. This property makes them highly electronegative.
- Non-metals are of many colors.
- Hydrogen is an exception that loses electron also and show both electropositive and electronegative properties.

➢ **Composition of non-metal:**

On earth crust: O>Si>Al>Fe>Ca

On ocean: O>H>Cl>Na>Mg

➢ **Physical properties:**

- **Strength and brittleness:** Non-metals are neither malleable nor ductile, they are brittle in solid state, they are generally soft (exception-diamond).
- **Electric and thermal conductivity:** Non-metals are bad conductor of electricity and heat(exception-graphite). This is because, covalent bonds of non-metals are shared by more than one atom, so no free electrons are present in lattice.
- **Density and luster:** Due to lacking of closed and dense packing in the lattice, they have a very low density. Non-metals are not lustrous, they are dull.
- **Melting and boiling points:** Non-metals have comparatively low melting and boiling points except diamond whose melting point is around 4000^0C.
- **Allotropy:** Some of the non-metals shows allotropy. For ex- carbon, phosphorus, sulfur, selenium.

Some exceptions:

- Iodine and Graphite are non-metals which are lustrous.
- Carbon's allotrope diamond is extremely hard and another allotrope graphite is a good conductor of electricity.
- Iodine has a high density of 4.9.

➢ **Chemical properties:**

- **Reaction with oxygen:** Non-metals react with oxygen to form acidic oxides or neutral oxides

  $C(s) + O_2(g) \rightarrow CO_2(g)$ (acidic oxide)

  The acidic oxide of a non-metal, dissolve in water to form acids. For ex-

  $CO_2 + H_2O \rightarrow H_2CO_3$ (carbonic acid)
- **Reaction with water:** Non-metals do not react with water or steam and hence **do not** emit hydrogen gas.
- **Reaction with dilute acid:** Non-metals do not react with dilute acid.
- **Reaction with chlorine:** Non-metals react with chlorine to form covalent chlorides which are non-electrolytes and do not conduct electricity. For ex-

  $H_2 + Cl_2 \rightarrow 2HCl$ (covalent chlorides)
- **Reaction with hydrogen:** Non-metals react with hydrogen to form covalent hydrides. For eg:

  $H_2 + S \rightarrow H_2S$ (covalent hydrides)
- **Electronegative nature:** Non-metals have 4 or 5 electrons in their outermost shells, so they form anions and become electronegative.

$N + 3e^- \rightarrow N^{3-}$

Note: exception of this property is hydrogen which shows both electropositive and electronegative nature as well. When hydrogen proceeds with alkali metals, it takes up one electron from them, making an H_2 molecule and hence showing electronegative nature. When it mixes with group 16 or 17 elements by losing its electrons to form H^+ ions and hence showing electropositive nature.

5.4 POSITION OF NON-METALS IN PERIODIC TABLE:

Elements toward left side of the periodic table are metals. When we move from left to right across a period, metallic property of element tends to decrease, thus non-metals are on the right side of the periodic table. However, some elements show some properties of metals as well as those of non-metals. These are called metalloids. Metalloids come between metals and non-metals. All non-metals are placed in p-block, except hydrogen which is in s-block.

Total number of non-metals= 22(17+5)

Non-metals= Hydrogen, Carbon, Nitrogen, Phosphorus, Oxygen, Sulphur, Selenium, Fluorine, Chlorine, Bromine, Iodine, Helium, Neon, Argon, krypton, Xenon, Radon,

Metalloids= Boron, Silicon, Germanium, Arsenic, Antimony, Tellurium

5.5 ORES:

Most metals are too reactive to exist on their own in the ground. Instead, they exist combined with other elements as compounds called ores. The deaired mineral or minerals together with the gangue (waste) constitute the ore, thus ore can be defined as a mineral aggregate containing one or more metals in profitable form. The minerals from which metals can be extracted economically are called ore. For ex. ZnS is an ore of zinc.

Difference between minerals and ores:

Minerals	Ores
They are inorganic substances that exist in Earth's crust	They are minerals from which one can extract metals economically.
They generally have definite crystalline structure	They generally do not Have definite structure
Not all minerals are ores	All ores are minerals
Metals cannot be extracted from all minerals	Metals can be extracted from all ores
Example: clay is mineral form of Aluminium	Example: Bauxite is an ore of Aluminium

- **Types of ores:**

The ores can be categorized in 4 types:

- Oxide ore: hematite (Fe_2O_3), corundum (Al_2O_3) etc.
- Carbonate ore: magnesite ($MgCO_3$), siderite ($FeCO_3$) etc.
- Sulphide ore: cinnabar (HgS), Galena (PbS) etc.
- Halide ore: horn silver (AgCl), cryolite (Na_3AlF_6) etc.

Note: metals are usually not found as nitrates in their ores (exception- Na, K); because metal nitrates are highly soluble in water.

Some metals and their ores:

S. No.	Metal	Ore	Chemical formula
1.	Sodium (Na)	Chile saltpetre	$NaNO_3$
		Trona	$Na_2Co_3.2NaHCO_3.3H_2O$
		Borax	$Na_2B_4O_7.10H_2o$
		Common salt	$NaCl$
		Glauber’s salt	$Na_2SO_4.10H_2O$
2.	Aluminium (Al)	Bauxite	$Al_2o_3.2H_2O$
		Corundum	Al_2o_3
		Feldspar	$KAlSi_3O_8$
		Cryolite	Na_3AlF_6
		Alunite (alum stone)	$KAl_3(SO_4)_2(OH)_6$
		Kaolin (China clay)	$3Al_2O_3.6SiO_2.2H_2O$
3.	Potassium (K)	Nitrate (saltpetre)	KNO_3
		Carnallite	$KCl.MgCl_2.6H_2O$
4.	Magnesium (Mg)	Magnesite	$MgCO_3$
		Dolomite	$MgCO_3.CaCO_3$
		Epsom salt	$MgSO_4.7H_2O$
		Kieserite	$MgSO_4.H_2O$
		Carnallite	$KCl.MgCl_2.6H_2O$
5.	Calcium	Dolomite	$CaCO_3.MgCO_3$
		Calcite (lime stone)	$CaCO_3$
		Gypsum	$CaSO_4.2H_2O$
		Fluorspar	CaF_2
6.	Copper (Cu)	Cuprite (Ruby copper/red glass)	Cu_2O
		Copper glance	Cu_2S
		Copper pyrites (chalcopyrite)	$CuFeS_2$
		Malachite	$CuCO_3.Cu(Oh)_2$
		Azurite	$Cu_3(CO_3)_2(OH)_2$
7.	Silver (Ag)	Ruby silver	Ag_3SbS_3
		Horn silver	$AgCl$
8.	Zinc (Zn)	Zinc blende	ZnS
		Zincite	ZnO
		Calamine	$ZnCO_3$
9.	Iron (Fe)	Hematite	Fe_2O_3
		Limonite	$2Fe_2O_3.3H_2O$

		Magnetite	Fe_3O_4
		Siderite	$FeCO_3$
		Iron pyrite	FeS_2
		Copper pyrites (chalcopyrite)	$CuFeS_2$
10.	Mercury (Hg)	Cinnabar	HgS
11.	Lead (Pb)	Galena	Pbs
		Cerussite	$PbCO_3$
		Anglesite	$PbSO_4$
12.	Nickel (Ni)	Millerite	NiS
13.	Manganese (Mn)	Pyrolusite	MnO_2
		Magnate	$Mn_2O_3.2H_2O$/ $MnO(OH)$
14.	Uranium (U)	Carnotite	$K(UO)_2.VO_4.3H_2O$
		Pitch blende	U_3O_8
15.	Cadmium (Cd)	Greenockite	CdS
16.	Barium (Ba)	Barytes	$BaSO_4$
17.	Gold (Au)	Calaverite	$AuTe_2$
		Sylvanite	$(Au.Ag)Te_2$
18.	Tin (Sn)	Cassiterite	SnO_2
19.	Bismuth (Bi)	Bismuthinite	Bi_2S_3
20.	Titanium (Ti)	Ilmenite	$FeTiO_3$
		Rutile	TiO_2
21.	Cobalt (Co)	Smelite	$COAsS_2$

Question:

1. The chemical formula of magnetite ore is: [MPPSC SFS Main 2020]
   - (a) $Fe_2O_3.\ 3H_2O$
   - (b) Fe_3O_4
   - (c) Fe_2O_3
   - (d) $CuFeS_2$
2. Which of the following is an ore of copper? [MPPSC SFS Main 2020]
   - (a) Siderite
   - (b) Malachite
   - (c) Kaolinite
   - (d) Calamine
3. Ruby copper is [MPPSC SFS Main 2021]
   - (a) Cu
   - (b) Cu_2S
   - (c) $Cu(OH)_2\ .CuCO_3$
   - (d) Cu_2O
4. Composition of siderite ore is [MPPSC SFS Main 2019]
   - (a) Fe_2O_3
   - (b) Fe_3O_4
   - (c) FeS_2
   - (d) $FeCO_3$
5. $MnO + 2C \rightarrow Mn + 2CO$ is the method of recovery for Manganese (Mn). Its principal mineral is? [MPPSC SFM SP 2019]
   - (a) Scheelite
   - (b) Wolframite
   - (c) Pyrolusite
   - (d) Haematite
6. Ilmenite and Rutile are principal ores of which metal? [MPPSC SFM SP 2019]
   - (a) Iron
   - (b) Titanium
   - (c) Nickel
   - (d) Copper
7. The chemical composition of copper glance is? [MPPSC SFM SP 2019]
   - (a) $CuFeS_2$
   - (b) $CuCO_3.\ Cu(OH)_2$
   - (c) Cu_1O
   - (d) Cu_2S
8. The chemical composition of Magnetite is? [MPPSC SFM SP 2019]
   - (a) Fe_2O_3
   - (b) Fe_3O_4
   - (c) $FeCO_3$
   - (d) FeS_2
9. The most important mineral of aluminium is: [MH Forest service Main 2019]
   - (a) Borax
   - (b) Kernite
   - (c) Bauxite
   - (d) Chalcopyrite
10. Match the following: [MH Forest service Main 2016]

Column-A	Column -B
(A) Haematite	1. Iron carbonate
(B) Magnetite	2. Hydrated iron oxide
(C) Limonite	3. Black ore
(D) Siderite	4. Oxide of iron

Answer option:

	(A)	(B)	(C)	(D)
(a)	4	3	2	1
(b)	3	4	1	2
(c)	1	2	3	4
(d)	2	1	4	3

11. Aluminium is extracted economically from the following ore: [MH Forest service Main 2016]
   - (A) Bauxite
   - (B) Malachite
   - (C) Dolomite
   - (D) Cryolite

   Which of the ores given are used?
   - (a) Malachite and Dolomite
   - (b) Bauxite and Cryolite
   - (c) Dolomite and Cryolite
   - (d) Bauxite and Dolomite

12. Cinnabar is an ore of: [CGPSC ACF 2020]
    (a) Lead
    (b) Zinc
    (c) Silver
    (d) Mercury

13. Among the following which are mismatched? [CG pariyojna 2021]
    (A) Acidic refractory material - Quartz
    (B) Basic refractory material – Bone ash
    (C) Reverberatory furnace – Smelting of tin stone
    (D) Millerite – Ore of copper
    (E) German silver – Alloy of silver
    Codes:
    (a) 2, 4 and 5
    (b) 1, 3 and 4
    (c) 1,2 and 3
    (d) 3, 4 and 5

14. Malachite is an ore of following metal [CGPSC ACF 2017]
    (a) Aluminium
    (b) Iron
    (c) Silver
    (d) Zinc
    (e) None of these

Answer Key

1. b	2. b	3. d	4. d	5. c	6. b	7. d	8. b	9. c	10. a	11. b	12. d
13. a	14. d										

Some important salts:

- Blue vitriol – $CuSO_4.5H_2O$
- White vitriol – $ZnSO_4.5H_2O$
- Green vitriol – $FeSO_4.7H_2O$
- Red vitriol – $CaSO_4.7H_2O$
- China clay – $Al_2O_3.2SiO_2.2H_2O$

5.6 ALLOYS:

When two or more elements are melted together and resulting liquid is allowed to solidify, the product so obtained is called an alloy, if it possesses metallic properties. An alloy may consist of a mixture of a metal with another metal, a metal with a non-metal or a metal with both metal and non-metal. Alloys are prepared because they have properties more suitable for certain applications than do the simple metals. Alloys are used because they are harder and stronger, have desirable casting properties, special physical properties such as magnetic properties and resistance to corrosion in certain environments. Melting point of an alloy is normally lower than the melting point of either of the pure components. Thermal and electrical conductivities are normally reduced in alloys.

- **Types:** Alloys are mainly classified into two distinct types, namely Ferrous and Non-Ferrous. Ferrous alloys always contain iron, carbon and one or two of the other elements such as manganese, nickel, chromium, copper, vanadium, molybdenum, tungsten, etc. When the percentage of carbon in the alloy is below 0.1%, the alloy is termed the iron alloy and if it is above 0.1%, the alloys are called steels. When iron is not present in the alloy, it is termed a non-ferrous alloy.

Another form of alloy is called amalgam, which is an alloy of mercury with another metal. It may be a liquid, a soft paste or a solid, depending upon the proportion of mercury. Almost all metals can form amalgams with mercury, the notable exceptions being Iron, Platinum, Tungsten.

Some of the important alloys are listed below:

Alloys	**Composition**	**Uses**
Brass	Cu + Zn	In making utensils, condenser tubes, electrical goods, cartridge shell etc.
Bronze	Cu + Sn	In making coins, bell and utensils, statues etc.
German silver	Cu + Zn + Ni	Utensils, resistance coils
Rolled gold	Cu + Al	Artificial jewellery
Gun metal	Cu + Sn + Zn	Guns, barrels, gears, and bearings.
Magnalium	Al + Mg	For making aircrafts and aeroplanes
Elektron	Mg + Al + Zn	Zeppelin airships, aircraft, and motor racing applications.
Dutch metal	Cu + Zn	Making artificial jewellery
Delta metal	Cu + Zn + Fe	Aeroplane blades and various applications in marine engineering like propellers, pump rods etc
Muntz metal	Cu + Zn	Used as boat sheathing, machine parts, elevator cabs, entrances, revolving doors etc
Rose metal	Bi + Pb + Sn	Used in soldering, Heating bath, Malleable filling to prevent tubes and pipes from crimping when bent
Duralumin	Al + Mg + Cu + Mn	In making aircrafts, pressure cooker etc
Solder	Pb + Sn	In soldering
Bell metal	Cu + Sn	Forecasting bells, gongs, and statues.
Stainless steel	Fe + Cr + Ni + C	For making utensils and surgical cutlery.
Britania	Sn + Sb + Cu	For making various utensils, including teapots, jugs, drinking vessels, candlesticks, urns, cutlery, and for official maces.
Wood's metal	Bi+ Pb + Sn + Cd	low-melting solder, low-temperature casting metal, high-temperature coupling fluid in heat baths, fire sprinkler systems, electric fuses and other safety devices
Nichrome (heater wire)	Ni+ Cr + Fe	used in heat producing devices such as iron toasters, hair dryer, electric ovens etc. fireworks and explosive industries. used in the ignition systems of rockets, electric matches, and electronic cigarettes.
Invar (alloyed steel)	Fe + C+ Ni	precision instruments, clocks, seismic creep gauges, television shadow mask, frames valves in engines and large aerostructure moulds, Surveying instruments, pendulums, chronometers.

Alnico	Al + Ni + Co	Used in making of permanent magnets, electric motors, electric guitar pickups, microphones, sensors, loudspeakers, magnetron tubes
Constantan (eureka)	Ni + Cu	Used for thermocouples, electrical resistance heating and DC current shunt
Spiegeleisen	Fe + C + Mn	Used in the manufacturing of steel in Bessemer's process
Dental alloy	Ag + Sn + Cu + Hg + Zn	Used for dentistry purposes

Questions

1. German silver is an alloy of copper and: [MPPSC SFS Main 2020]
   (a) Zn + Al
   (b) Sn + Al
   (c) Zn + Ni
   (d) Sn + Ni
2. Brass is an alloy of following metals [MPPSC SFS Main 2019]
   (a) Cu and Zn
   (b) Cu and Sn
   (c) Cu and Ni
   (d) Cu, Sn and Ni
3. Which alloy steel is used for the preparation of permanent magnets? [MPPSC SFS Main 2019]
   (a) Chrome steel
   (b) Nickel steel
   (c) Alnico
   (d) Stainless steel
4. Which among the following alloys contains Tin (Sn) as some of its constituents? [MPPSC SFM 2018]
   (a) Stainless Steel
   (b) Brass
   (c) Bronze
   (d) German Silver
5. Match List -I with List -II and select the correct answer using following codes: [CG pariyojna 2021]

List -I	List -II
(A) Invar	1. High tensile strength
(B) Chrome vanadium steel	2. Hard and tough
(C) Alnico	3. Corrosion resistant
(D) Manganese steel	4. Highly magnetic
(E) Stainless steel	5. Very small coefficient of expansion

Code

	(A)	(B)	(C)	(D)
(a)	1	2	3	4
(b)	5	4	3	2
(c)	3	2	1	4
(d)	5	1	4	2

6. An alloy of iron and Nickel is called [CG labour inspector 2015]
   (a) Brass
   (b) Invar
   (c) Bronze
   (d) None of the above

Answer Key

1. c	2. a	3. c	4. c	5. d	6. b				

CHAPTER

6

METALLURGY

Syllabus: introduction, steps involved in the extraction of metals: concentration (gravity separation, magnetic separation, froth flotation), conversion of ores into oxide (calcination, roasting), reduction of ore (different processes), metallurgy of Copper and Iron, corrosion of metals.

6.1 INTRODUCTION

The branch of chemistry which deals with the study and practice of extraction of metals from their ores, refining them for use, and creating alloys is called metallurgy. It is a crucial field that has played a pivotal role in the development of human civilization, shaping various industries and technological advancements.

Mineral: The various compounds of metals which occur in the earth's crust and are obtained by mining are called minerals. In earth crust, order of abundance of elements is. O > Si > Al > Fe

A mineral may be single compound or a mixture of compounds having fixed chemical composition.

Gangue: The undesirable impurities present in an ore are called gangue. It is also known as matrix.

Flux: flux refers to a substance or mixture used to promote the fusion of metals or minerals during the smelting process. The purpose of using flux is to lower the melting point of the raw materials, facilitating the removal of impurities, and promoting the separation of slag from the metal.

Types: depending upon the process, metallurgy has 4 types:

a) Pyro metallurgy: Extraction of metal from ore by using heat energy. Steps involved are: Calcination, roasting, reduction etc. Ex. Less reactive metals: Cu, Fe, CO, Ni, Zn, Sn, Pb etc.

b) Hydro metallurgy: (for Ag, Au) this is wet metallurgy process.

Cu → Pyro + Hydro

Ag and Au → By cyanide process.

c) Electrical metallurgy: this process is used for highly electropositive materials (S-block & Al). Metal obtained by electrolysis of fused salt/anhydrous medium.

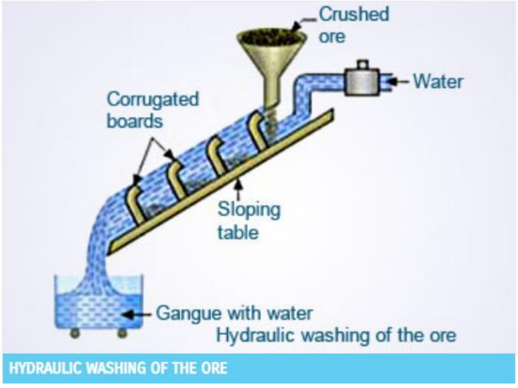
d) Ion exchange metallurgy: trans-uranic (elements after uranium in periodic table) elements are obtained by this method.

6.2 STEPS INVOLVED IN THE EXTRACTION OF METALS:

The extraction is completed in following steps:

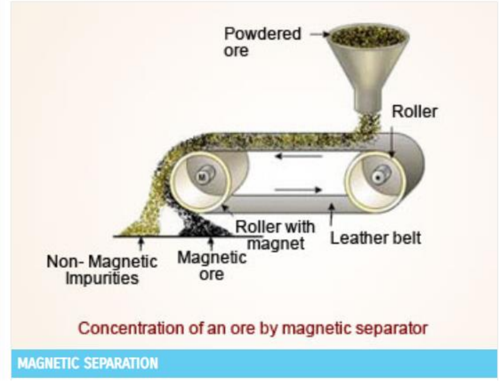
- **Crushing and grinding (Pulverization):** Operation in which size reduction of large lumps to small pieces followed by finely ground material is done by using crushers and grinders. Hand picking of selective pieces of ores is also done here.

- **Concentration of the ore:** Operation in which the removal of impurities (gangue) from ore by following method:
  - **Gravity separation (levigation):** This method of concentration of the ore is based on the difference in the specific levigation gravities of the ore and the gangue particles. Powdered ore is agitated with a running stream of water. The lighter gangue particles are taken away by water while heavier ore particles settle down. Ex. Generally oxides and carbonate ores are concentrated by this method.



HYDRAULIC WASHING OF THE ORE

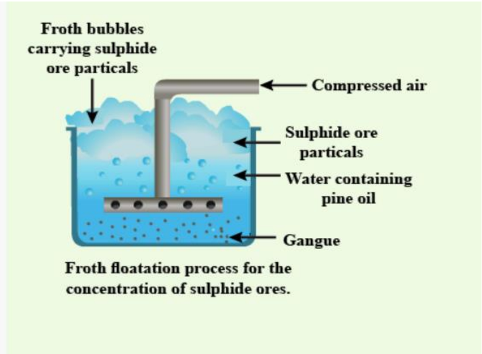
  - **Magnetic separation:** ore and gangue are separated, if only one of them is having magnetic property. For ex. In metallurgy of iron (fe), ore is magnetic and impurity is non- magnetic, but in metallurgy of tin (Sn), ore (SnO_2) is non-magnetic and impurity wolframite ($FeWO_4$) is magnetic. Powered ore is slowly push forward in a conveyer belt with magnetic wheels. The impurity separates earlier and the ore separates after that because of magnetic wheel.



Concentration of an ore by magnetic separator

MAGNETIC SEPARATION

  - **Froth floatation:** This method is mainly employed for the concentration of sulphide ores. The method is based on the different wetting characteristics of the gangue and the sulphide ore with water and oil. The gangue preferentially wetted by water and the ore by oil. The crushed ore along with water is taken in a floatation cell. Various substances are added depending on the nature of the ore. Ore particles raised to the surface along with air bubbles and collected at the surface whereas gangue particles are wetted and settled down at the bottom of the tank. The substances added are usually of three types:



Froth floatation process for the concentration of sulphide ores.

- (a) Froathers: They generate a stable froth which rises to the top of the tank. Example of frother is pine oil, Eucalyptus oil, etc.
- (b) Collectors: These attach themselves by polar group to the grains of the ores which then become water repellent and pass on into the froth. Example: sodium ethyl xanthate and potassium ethyl xanthate.
- (c) Activators or depressants: These compounds activate or depress the floating property of one of the components of the ore and thus help in separation of different minerals present in the same ore. An example of depressant is NaCN, an activator is CuSO4.

➢ **Leaching:** Some of the ores are concentrated by means of chemical treatment, i.e., leaching. It involves the treatment of the ore with a suitable reagent. as to make it soluble while impurity remain insoluble(hydrometallurgy). The ore is recovered from the solution by suitable chemical method. This method is used for ores of aluminium, silver, gold:

a) Bayer's process- bauxite ore (containing impurity of fe_2O_3, SiO_2) is concentrated by this process.

b) Cyanide process- silver, gold is treated by this (Mac-Arthur Forest cyanide process).

Exercise 1	
1. Copper pyrite is concentrated by the method [CGPSC ACF 2017] (a) Froth floatation process (b) Electromagnetic method (c) Gravity separation method (d) All of the above are correct (e) None of these	2. Ores that are concentrated by Froth Flotation method are: [MPPSC SFM 2018] (a) Carbonate ores (b) Sulphide ores (c) Oxide ores (d) Phosphate ores
(1.) a, (2.) b	

Now the concentrated ore is **converted into its oxide** form by using following methods:

i. Calcination: Calcination is a process in which ore is heated, generally in the absence of air, to expel water from a hydrated oxide or carbon dioxide from a carbonate at temperature below their melting points. During this process volatile impurities and moisture are expelled and ore becomes porous. Calcination is used only for oxide and carbonate ores. For ex.

➢ $Al_2O_3.\,2H_2O \longrightarrow Al_2O_3 + 2H_2O$

➢ $2Fe_2O_3.3H_2O \longrightarrow 2Fe_2O_3 + 3H_2O$

➢ $CaCO_3 \longrightarrow CaO + CO_2$

➢ $MgCO_3 \longrightarrow MgO + CO_2$

ii. Roasting: (Metal sulphides $\longrightarrow$ Metal oxide + SO_2)

The removal of the excess sulphur contained in sulphide ores(only) by heating in an excess of air is called roasting. The concentrated sulphide ore is heated in reverberatory furnace, below its melting point or fusion temperature in the presence of an excess of air with or without the addition of an external substance. In roasting definite chemical changes like oxidation, chlorination etc. take place but in calcination, any major chemical changes do not occur. Some of the impurities also expelled as volatile substances and ore becomes porous.

- $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$ (conversion into oxide)
- $2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$ (same as above)
- $ZnS + 2O_2 \longrightarrow ZnSO_4$ (conversion into sulphate)
- $PbS + 2O_2 \longrightarrow PbSO_4$ (same as above)

- **Reduction of ore to the metal:** The calcined or roasted ore is then reduced to the metallic state in either of the following ways:

(a) Reduction by carbon(smelting): Reduction of the oxide with carbon at high temperature is known as smelting. The oxides of less electropositive metals like Pb, Zn, Fe, Sn, Cu etc. are reduced by strongly heating them with coal or coke, in the blast furnace. Flux is added during smelting, which reduces the melting point of impurities to form an easily fusible substance called as 'slag' and can be separated easily because of its lower density. Selection of flux depends upon nature of impurity present, if impurity is acidic, then basic flux is used and vice-versa.

Acidic fluxes: Borax, SiO2 (remove basic impurity)

basic fluxes: MgO, $MgCO_3$, $CaCO_3$ (remove acidic impurity)

some examples:

- $CuO + CO \longrightarrow CO_2 + Cu$
- $PbO + C \longrightarrow Pb + CO$
- $SiO_2 + CaCO_3 \longrightarrow CaSiO_3 + CO_2$ ($CaCO_3$ is basic flux to remove acidic impurity)
- $MgCO_3 + SiO_2 \longrightarrow MgSiO_3 + CO_2$ (SiO_2 is acidic flux to remove basic impurity)

Note:

(1) In Cr_2O_3, Mn_3O_4, MnO_2; carbon is not used for reduction because these metals (Cr and Mn) have higher affinity for oxygen.

(2) Coke is not used for reduction of S-block oxide Al_2O_3, due to formation of metal carbides.

(3) Blue flame is obtained by burning of CO in smelting process.

(b) Self-Reduction: Compounds of certain metals are reduced to metal without using any additional reducing agent. ores of Cu, Pb, Hg etc. Their sulphide ores are partially roasted to give some oxide. This oxide is now reduced to the metal by the remaining sulphide ore at elevated temperatures in the absence of air. The process is known as Self Reduction.

For ex: $PbS + 2PbO \xrightarrow{high\ temp.} 3Pb + SO_2$ (Self reduction in absence of air)

(c) Metal displacement method (Precipitation): In this method, a water-soluble compound is obtained from the ore. The aqueous solution of the compound is reacted with a more electropositive metal which displaces the metal from the solution. For ex:

- $Ag_2SO_4\,(aq) + Cu \rightarrow CuSO_4\,(aq) + 2Ag\,(S)$ [Zairvogel process for silver]

- $CuSO_4 + Fe \rightarrow FeSO_4 + Cu$
- $Ag_2S + 4NaCN \xrightarrow{air} 2Na[Ag(CN)_2] + Na_2SO_4$
- $2Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4]\ (aq) + 2Ag\downarrow$ [Cementation]

Note: {$ZnSO_4 + Cu$} will not happen because zinc is more reactive than copper, hence copper will not be able to displace zinc.

(d) Electrolytic reduction: This process is mainly used for the extraction of highly electropositive metals. Electrolysis is carried out in a large cell and a small amount of another suitable electrolyte is added which lowers the melting point of main electrolyte, enhances its conductivity, and reduces corrosion troubles. For ex. Na, K, Mg, ca, Al. Manufacture of metallic sodium (Down's process) is also done by electrolysis in which molten NaCl containing a little $CaCl_2$ is electrolyzed between graphite anode and iron cathode.

Fusion: $2NaCl \leftrightharpoons 2Na^+ + Cl^-$

Electrolysis: Cathode: $Na^+ + e^- \rightarrow Na$ (reduction)

Anode: $2Cl^- \rightarrow Cl_2\ (g) + 2e^-$

(e) Reduction by aluminium: Aluminium acts as reducing agent due to its highly electropositive nature. Oxides which are not reduced by carbon or carbon monoxide, such as Cr_2O_3 and Mn_3O_4, are reduced by this process. This process is also known as 'Gold-Schmidt thermite process.'

- $Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$
- $3Mn_3O_4 + 8Al \longrightarrow 9Mn + 4Al_2O_3$

Exercise 2

1. When Iron rod is dipped in copper sulphate solution, copper is displaced and it gets deposited of Iron rod because [Raj ACF 2018]
   (a) Atomic number of Fe < Cu
   (b) The standard reduction potential of copper is more than iron.
   (c) The standard reduction potential copper is less than iron.
   (d) The iron salt has more solubility than copper salt.

(1) b

- **Refining of the metal:** Metals obtained by the reduction of its compound still contains some objectionable substance (like Si, P, slag etc.) and must be refined. Depending upon the nature of the metal and impurities, the following methods are used for purification of the metals:

  a) Liquation: This method is used for the refining of metals having high melting impurities and low melting points Ex. Pb, Sn, Sb, Bi and Hg. The impure metal is heated on the sloping hearth of a furnace. Pure metal flows down leaving behind the non-fusible material on the hearth.

  b) Distillation: Metals having low boiling point are refined by this method, for example, zinc, cadmium, and mercury.

c) Zone refining or fractional crystallisation: Metals of very high purity (semiconductors) are obtained by zone refining This refining method is based on the fact, that impurities tend to remain dissolved in molten metal. Elements that are refined by this are silicon, germanium, and gallium.

d) Electrorefining: highly electropositive metals such as Cu, Ag, Zn, Sn, Pb, Al, Ni, Cr are refined by this method. The impure metal is made the anode of an electrolytic cell, while cathode is thin plate of pure metal. Electrolyte is the solution of a double salt of the metal. On passing the electric current pure metal from the anode dissolves and gets deposited at the cathode. The soluble impurities go into the solution while insoluble or less electropositive impurities settle down below the anode as anode mud or sludge.

Note:

- Faraday's first law of electrolysis: according to this law, the chemical deposition caused by the flow of current through an electrolyte is proportionate to the amount of electricity passing through it. Its formula is:

  M α Q [M is the mass of the ions formed or reacted]
  M = ZQ [Q is the electric current]
  M = Zit [Z is the electrochemical equivalent mass of 1-coulamb charge]
  Here M can be written as W also.

- Faraday's second law of electrolysis: Faraday's second law of electrolysis states that- if the same amount of electricity is passed through different electrolytes, the masses of ions deposited at the electrodes are directly proportional to their chemical equivalents. Mathematically: $\frac{W1}{W2} = \frac{E1}{E2}$ or Z α E

e) Van-Arkel process: Employed to get metal in very pure form of small quantities. In this method, the metal is converted into a volatile unstable compound (ex. iodide), and impurities are not affected during compound formation. The compound thus obtained is decomposed to get the pure metal. Employed for purification of metals like titanium (Ti) and zirconium (Zr).

- $Ti(s) + 2I_2(g) \xrightarrow{523k} TiI_4(g)$
- $TiI_4(g) \xrightarrow{1700\ k} Ti(s) + 2I_2(g)$

f) Oxidation process: These processes are used for refining of metals associated with impurities having high affinity for oxygen than the metal itself. Cupellation (for Ag), pudding and bessemerization are important oxidation processes employed for refining different metals.

- Cupellation: The process in which an impure sample of metal (say Pb in Ag) is fused in a bone ash crucible (cupel) on the hearth of a furnace in the blast of the air is known as cupellation. The impurity (Pb) present, is oxidized and blown away with air. The process is based on the principle that precious metals do not oxidise or react chemically, unlike base metals. When they are heated at high temperatures, the precious metals remain apart, and the others react, forming slags or other compounds.

Exercise 3

1. When an impurity in metal has greater affinity for oxygen and is more easily oxidized, then the metal is refined by [CG Vyapam RFO 2021]
   - (a) Electrolytic process
   - (b) Zone refining
   - (c) Bessemerisation
   - (d) Cupellation
2. Which of the following methods is used to remove lead present in silver? [CGPSC ACF 2020]
   - (a) Distillation
   - (b) Cupellation
   - (c) Poling
   - (d) Liquation
3. Mathematical expression of Faraday's First law of electrolysis is ___ [MHPSC forest Main 2021]
   - (a) $W = Q, W = Z x I x t, W = ZQ$
   - (b) $W= Q, W =Z x Q, W \alpha Q$
   - (c) $W \alpha Q, W = Q, W = Z x I X t$
   - (d) $W = Z x I x t, W = Z X Q, W \alpha Q$
4. Which of the following method is used for extraction or refining of metals? [MPPSC SFM SP 2019]
   - (a) Electrolysis
   - (b) Vapour phase refining
   - (c) Zone refining
   - (d) All of the above
5. Match the following: [MPPSC SFS Main 2021]

(A) Calcination	1. Presence of air
(B) Roasting	2. Pine oil
(C) Smelting	3. Absence of air
(D) Frothing agent	4. Reduction of metal oxide

Codes

	(A)	(B)	(C)	(D)
(a)	3	1	2	4
(b)	1	3	2	4
(c)	1	2	3	4
(d)	3	1	4	2

(1.) d, (2.) b, (3) d, (4) d, (5) a

6.3 METALLURGY OF COPPER:

Metallurgy of copper involves several stages and processes to extract pure copper from its ores. The three main types of copper ores are sulphide ores, oxide ores and carbonate ores:

- Sulphide ore: Cu_2S (copper glance), $CuFeS_2$ (copper pyrite)
- Oxide ore: Cu_2O (Cuprite or Ruby copper)
- Carbonate ore: $CuCO_3.Cu(OH)_2$ [malachite]

Here is a general overview of the metallurgical process for extracting copper from these ores:

(a) Concentration: after mining, the crushed and grounded ore is then subjected to a process called froth floatation. In this process, the ore particles cling to bubbles and float on the surface, separating from the non-copper bearing minerals. Chemicals called collectors are added to the mixture to enhance the floatation process.

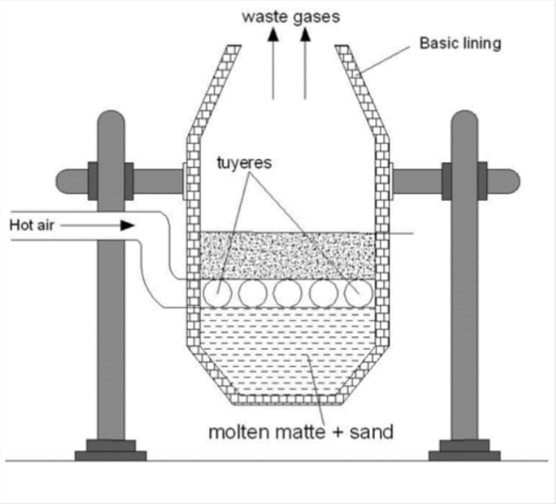
(b) Roasting: concentrated ore is heated in induction furnace below melting point, through hot air. Sulphur, phosphorus, arsenic, and antimony are removed as oxides. Copper pyrite is partly converted into copper and iron sulphides and then converted into oxides.

- $2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$
- $2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$
- $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$

(c) Smelting: the roasted ore is then combined with coke and sand (this mixture is called 'charge') and then heated in blast furnace to produce 'matte' (Cu_2S+ FeS). Further ferrous oxide (FeO) reacts with silica and form slag. Molten mass collected from the bottom of furnace contains largely cuprous sulphide and a little ferrous sulphide. This molten mass is known as matte or copper matte.

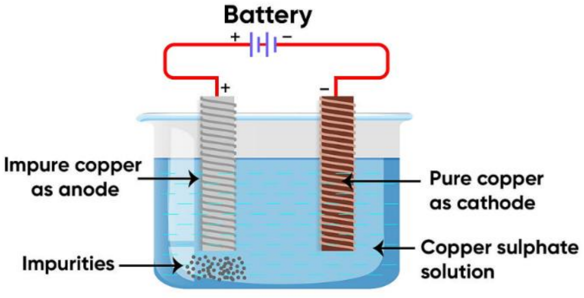
- $Cu_2O + FeS \longrightarrow Cu_2S + FeO$
- $FeO + SiO_2 \longrightarrow FeSiO_3$ (slag)

(d) Bessemerization: The molten matte is finally transferred to Bessemer converter. A blast of sand and air is blown in the converter through tuyeres which are situated a little above from the bottom. This causes removal of Sulfer as oxides and ferrous oxide as slag. At the same time Cu_2S is oxidized mostly into Cu_2O, all these react with Cu_2S giving copper. The sulphur dioxide gas exits during this and leave blisters on copper, hence the obtained copper is known as blister copper with 98% purity.



- $2Cu_2S + 3O_2 \longrightarrow 2\,Cu_2O + 2SO_2 \uparrow$
- $2Cu_2S + 5O_2 \longrightarrow 2CuSO_4 + 2CuO$
- $2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2 \uparrow$
- $CuSO_4 + Cu_2S \longrightarrow 3Cu + 2SO_2 \uparrow$

(e) Refining: as blister copper contains 2% impurities, it is then purified by electrolytic refining. In this process a large thick piece of impure copper is used as anode and a thin strip of pure copper is used as cathode. Copper sulphate solution is used as electrolyte.



When an electric current is passed through the electrolyte, copper ions are transferred from the anode to the cathode, forming pure copper metal at the cathode. Impurities settle at the bottom of the electrolytic cell as anode sludge/mud, which contains antimony, selenium, tellurium, silver, gold, and platinum.

The purified copper, now in the form of cathodes, is removed from the electrolytic cell and cast into shapes such as plates or rods. These shapes can be further processed into various products like wires, tubes, and sheets, which are used in different industries.

Exercise 4

1. "Copper matte" mainly contains [CGPSC ACF 2017]
   (a) Cu_2O and FeO
   (b) Cu_2S and FeS
   (c) Cu_2O and FeS
   (d) Cu_2S and FeO
2. During the process of electrorefining of copper, the anode mud contains [CG Vyapam RFO 2021]
   (a) Sn and Ni
   (b) Pb and Zn
   (c) Fe and Ni
   (d) Ag and Au
3. The products of the reaction between metallic copper and hot concentrated sulphuric acid are: [MH Forest service Main 2019]
   (a) $CuSO_4 + H_2$
   (b) $CuSO_4 + SO_2 + H_2O$
   (c) $CuO + H_2O + SO_2$
   (d) None of these
4. Which of the following is a slag? [MPPSC SFS Main 2019]
   (a) FeO
   (b) CaO
   (c) SiO_2
   (d) $FeSiO_3$
5. During the extraction of copper from cuprous oxide, blisters appeared on the surface of solidified copper is due to: [MPPSC SFS Main 2020]
   (a) Elimination of hydrogen gas
   (b) Elimination of carbon dioxide gas
   (c) Elimination of carbon mono oxide gas
   (d) Elimination of sulphur dioxide gas

(1.) b, (2.) d, (3) b, (4) d, (5) d

6.4 METALLURGY OF IRON:

Metallurgy of iron involves several stages and processes to extract pure iron from its ores. The three main types of iron ores are sulphide ores, oxide ores and carbonate ores:

- Oxide ore: hematite (Fe_2O_3), magnetite (Fe_3O_4)
- Carbonate ore: siderite ($FeCO_3$)
- Sulphide ore: iron pyrite (FeS_2), copper pyrite ($CuFeS_2$)

Here is an overview of the metallurgy of iron:

(a) Concentration: the ore obtained from mining is subjected to some concentration process depending upon its nature. Hematite is concentrated by hydraulic washing or gravity separation, while magnetite is concentrated by magnetic separation. In gravity separation ore is agitated with a running stream of water and the lighter gangue particles are taken away by water while heavier ore particles settle down. Whereas in magnetic separation, the ore is push forward in a conveyer belt with magnetic wheel, which separates the magnetic ore.

(b) Calcination and Roasting: the concentrated ore roasted and calcined in with a little coal in a shallow kiln in excess air, following changes takes place during this process:

- Moisture is removed as steam and organic matter burns off to give CO_2.
- Impurities like P, S, As, etc are removed as their volatile oxides.
- Ferrous oxide is converted into ferric oxide, which avoids formation of ferrous silicate in slag during smelting.
- The molten mass becomes porous and thus makes it more suitable for reduction to metallic iron. Reactions are as follows:
- $Fe_2O_3.3H_2O \rightarrow Fe_2O_3 + 3H_2O$
- $FeCO_3 \rightarrow FeO + CO_2$
- $4FeO + O_2 \rightarrow 2Fe_2O_3$

(c) Smelting: The roasted and calcined ore (8 parts) is mixed with coke (4 parts) [which acts as a reducing agent]and limestone (1 part) [which acts as a flux]. The mixture (known as charge) is introduced in a tall Blast Furnace. The blast furnace has two functions, first is to reduce the ore to metallic iron and second is to remove the impurities in the form of slag.

- The mouth of the furnace i.e. the top is closed by a double cup and cone arrangement through which the mixture (called charge) of the calcined ore, limestone and coke is fed from time to time. The hot gases escape from here.
- A blast of hot and dry air, obtained by hot gases, escaping from the blast furnace itself and freed from dust in a scrubber, is blown into the furnace, just above the hearth with number of water-cooled pipes, called tuyeres (pipe rings).
- Near the bottom of the furnace, there are two outlets on opposite sides, one for the removal of slag (called slag hole) and the other for taking out molten metal (called metal hole or tap hole). The reactions take place during this are as follows:

i. Zone of reduction: ($300^0C – 800^0C$/dull red heat) This is the uppermost zone of the blast furnace. It is called the zone of reduction. Here the iron oxide from the charge is reduced by carbon monoxide to spongy iron.

$Fe_2O_3 + 3CO \rightarrow 2Fe$ (spongy iron) $+ 3CO_2\uparrow$

$3Fe_2O_3 + CO \rightarrow CO_2 + 2Fe_3O_4$

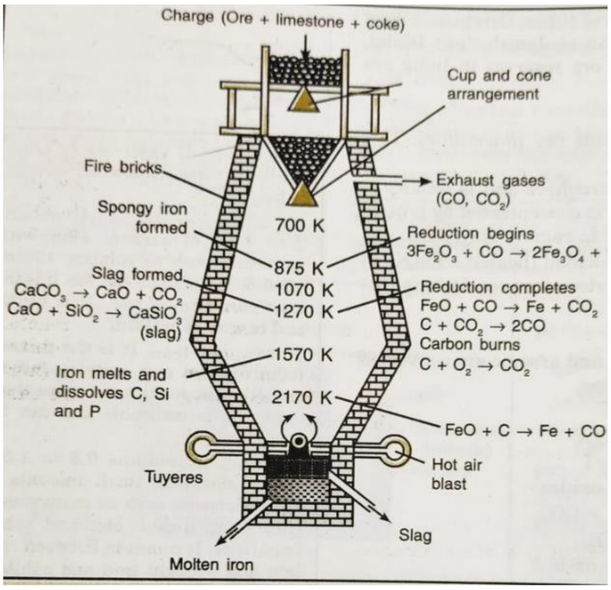
$Fe_3O_4 + CO \rightarrow CO_2 + 3FeO$

$FeO + CO \rightarrow CO_2 + Fe$

ii. Zone of slag formation: (800^{0}C-1000^{0}C/bright red heat) When the spongy iron falls in the middle region (zone of heat absorption), limestone (CaCO3) decomposes to give CaO (lime) and CO_2. Lime thus obtained acts as a flux. It combines with silica to form a fusible (meltable) slag.

$CaCO_3 \rightarrow CaO + CO_2$

$CaO + SiO_2 \rightarrow CASiO_3$ (slag)



iii. Zone of combustion: (1300^{0}C-1500^{0}C/white heat) This is the zone near the tuyeres. Here the carbon burns to form CO_2 producing tremendous amount of heat.

$C + O_2 \rightarrow CO_2 \uparrow + 97$ kcal

iv. Zone of fusion: (1500^{0}C-1900^{0}C) In this zone, the spongy iron melts and dissolves some carbon, phosphorus, and silica. The molten iron collects at the bottom of the furnace while the fusible slag floats on it and protects the iron from oxidation. The layers of molten iron and slag are withdrawn through separate tapping holes from time to time.

Iron so obtained is known as Pig Iron. It is remelted in a vertical furnace (known as cupola) and can be cast or poured into moulds. It is then called cast iron. So cast iron is obtained after remelting pig iron.

Exercise 5

1. The oxides of iron ore are reduced in the blast furnace at lower temperature range 500-800K. this reduction is due to [MPPSC SFS Main 2020]
   (a) C
   (b) CO_2
   (c) CO
   (d) Silica
2. Consider the following statements:
   Coke is one of the materials of charge added to blast furnace for production of steel/iron. Its function is to [CG pariyojna 2021]
   (A) Acts as the reducing agent.
   (B) Removes silica associated with iron use.
   (C) Functions as fuel to supply heat.
   (D) Acts as an oxidising agent.
   Correct statements are:
   (a) 1 and 2
   (b) 2 and 4
   (c) 1 and 3
   (d) 3 and 4

(1.) c, (2.) c

6.5 CORROSION OF METALS:

Corrosion is a natural process that occurs when metals react with their environment. It is a destructive phenomenon that can cause significant damage to structures, machines, and equipment. "The gradual destruction of pure metals by the action of air, moisture or a chemical (like an acid) on their surface is called corrosion." Most of the metals corrode when they are kept exposed to damp air (moist air). For ex.

- The copper objects lose their shine after sometime due to the formation of copper oxide on them. When a copper object reacts with moist carbon dioxide (CO_2), it loses its shiny brown surface and gains a green coat. This greenish coat is a basic copper oxide which is a mixture of copper carbonate and copper hydroxide.
- Silver articles became black after sometime when exposed to air because it reacts with sulphur in air to form a coating of silver sulphide.

Corrosion of iron: when an iron object is left in damp air (or water) for a considerable time, then it reacts with oxygen in the catalytic presence of water or air moisture and form a reddish-brown flaky substance called rust. Rust is hydrated iron oxide with formula $Fe_2O_3.XH_2O$; the two conditions essential for rusting of iron is presence of air and water.

Electro-chemical theory of rusting: Electrochemical corrosion of metals occurs when electrons from atoms at the surface of the metal (iron) are transferred to a suitable electron acceptor or depolarizer. Water must be present to serve as a medium for the transport of ions. Most common depolarizers are oxygen, acids, and the cations of less active metals. Rust behaves like miniature electrochemical cell:

i. At anode, iron (Fe) undergoes oxidation to release electrons.
   $Fe \rightarrow Fe^{+2} + 2e^-$ (oxidation half-reaction)
ii. Oxygen from the air can gain electrons to form hydroxide ions:
   $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (reduction half-reaction)
iii. Net reaction:
   $2Fe + 4H^+ + O_2 \rightarrow 2Fe^{+2} + 2H_2O$
   Now ferrous ion oxidized by atmospheric oxygen and form rust:
   $4Fe^{+2} + O_2 + 4H_2O \rightarrow 2Fe_2O_3 + 8H^+$
   $Fe_2O_3 + XH_2O \rightarrow Fe_2O_3.\ XH_2O$ (hydrated ferric oxide/Rust)

Factors affecting corrosion:

i. Nature of metals: more reactive the metal is, more corrosion would occur.
ii. Presence of impurities: presence of impurities in metals increase the occurrence of corrosion.
iii. Atmospheric conditions: moisture, air, CO_2 etc increase the rate of corrosion.
iv. Presence of electrolyte: Substances that enhance the electrical conductivity of a solution, such as salts and acids, can accelerate corrosion by providing a medium for the flow of ions.

Note: When mercuric chloride ($HgCl_2$) is heated, it sublimates and has corrosive action. Hence it is known as corrosive sublimate. It is also an oxidizing agent; it oxidizes the stannous chloride.

v. Ph level: The acidity or basicity of the environment, as measured on the pH scale, can influence corrosion. Acids generally accelerate corrosion (ph 3 or below), while some bases can also be corrosive under certain conditions.

vi. Biological factors: Corrosion can also be caused or accelerated by microorganisms, such as bacteria, fungi, and algae, which produce corrosive byproducts.

Prevention from corrosion: there are several preventive measures to protect metals from corrosion. These methods can be applied individually or in combination, depending on the specific requirements and the environment in which the metal is placed.

1. Barrier protection:
    - By applying paint/oil/grease/enamel on the surface
    - Using electroplating method (layering of Cu/Sn/Ni/Zn)
    - Using anodizing process (layering of Al)
2. Galvanization: Coating iron or steel with a layer of zinc through a process called galvanization. It can protect the underlying metal from corrosion. Zinc acts as a sacrificial anode, corroding preferentially to the iron or steel.
3. Using antirust solution: basic phosphate and basic chromate solution is used for preventing rust. Ex. sodium phosphate (Na_3PO_4) solution.
4. Alloying: Creating alloys by mixing metals with other elements can improve their corrosion resistance. Stainless steel, for instance, contains chromium, which forms a passive oxide layer, protecting the underlying metal from corrosion.
5. Controlled environment: Storing metal objects in a controlled environment with low humidity and temperature can prevent corrosion. This is often applied in museums and archival storage facilities.

Exercise 6

1. Galvanisation is a method of protecting iron from rusting by coating with thin layer of a metal, which of the following metal us use for this purpose [MPPSC SFM 2018]
   - (a) Copper
   - (b) Aluminium
   - (c) Zinc
   - (d) Chromium
2. In galvanisation, the surface of iron is covered by following metal [MPPSC SFS Main 2019]
   - (a) Ni
   - (b) Zn
   - (c) Sn
   - (d) Cu
3. Corrosive sublimate is [CGPSC ACF 2020]
   - (a) Mercurous chloride
   - (b) Mercuric chloride
   - (c) Ferrous chloride
   - (d) Ferric chloride

(1.) c, (2.) b, (3) b

CHAPTER

7

PREPARATION AND PROPERTIES OF HYDROGEN, OXYGEN, AND NITROGEN

Syllabus: hydrogen: preparation, isotopes, types, properties and uses; oxygen: preparation, properties and uses; nitrogen: preparation, properties and uses; alcohol: preparation, types, properties and uses; acetic acid: preparation, properties and uses.

7.1 HYDROGEN

Hydrogen is the first and the lightest element in the periodic table. It was discovered by Henry Cavendish in the 18th century. It occurs rarely in free state because it is highly reactive. It is the most abundant element in the universe (70% of the total mass of the universe.), the earth's crust contains 1% of hydrogen by weight. Important sources are water, acids, alkalis, organic matter etc.

Position in periodic table: the position of hydrogen is not definite in the periodic table because it resembles both the alkali metals (group 1st/IA) as well as halogens (17th/VIIA). At the same time, it differs from both in many characteristics.

Isotopes of hydrogen:

Name	**Protium** (ordinary hydrogen)	**Deuterium** (heavy hydrogen)	**Tritium** (radioactive)
Symbol	$_1H^1$	$_1H^2$	$_1H^3$
Neutrons	0	1	2
Protons	1	1	1
Electrons	1	1	1
Stability	Stable	Stable	Unstable (radioactive)
Electronic configuration	$1S^1$	$1S^1$	$1S^1$

Methods of preparation: there are several methods of preparing hydrogen:

1. By action of metals with acid: The metals which are placed above H_2 in electrochemical series, react with dilute acids and liberate hydrogen.

$Fe + H_2SO_4(dil) \rightarrow FeSO_4 + H_2$

$Zn + 2HCl\ (dil) \rightarrow ZnCl_2 + H_2$

Note: (a) pure zinc is not used during this preparation.

(b) concentrated H_2SO_4 is not used as it oxidizes the liberated H_2 and produce SO_2.

2. By alkalis: Only (Be, Zn, Al, Sn, Pb, Si) (Amphoteric metals) react with boiling NaOH or KOH and they evolve H_2.

$Zn + 2NaOH \rightarrow Na_2ZnO_2$ (sodium zincate) $+ H_2\uparrow$

$2Al + 2NaOH + 2H_2O \longrightarrow NaAlO_2$(sodium meta-aluminate) $+ 3H_2\uparrow$

3. By action of water: metals which are placed above H_2 in electrochemical series, evolve H_2 when react with water:

$Zn + H_2O \longrightarrow ZnO + H_2\uparrow$

Note: three types of water are used:

- Cold water: highly reactive metals like Li, Na, K, Ca, Sr
- Hot water: with reactive metals like Mg, Al, Mn, Zn, Cr
- Steam: with less reactive metals like Fe, Cd, Co, Ni, Sn, Pb

4. By electrolysis of water: to prepare pure hydrogen, we use impure water (having 15% solution of alkali or acid):

$4H_2O \rightleftharpoons 4H^+ + 4OH^-$

At cathode: $4H^+ + 4e^- \longrightarrow 2H_2$

At anode: $4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$

5. Uyeno method: this method is used for military purposes because by this, we can prepare H_2 in a rapid manner.

$2Al + 2KOH + 2H_2O \longrightarrow 2KAlO_2$ (potassium meta-aluminate) $+ 3H_2\uparrow$

6. Industrial methods:

i. Lane's process: steam is passed over hot iron and this gives magnetic oxide (Fe_3O_4) and hydrogen. This reaction is termed as gassing reaction.

$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$

Iron is regenerated by reducing Fe_3O_4 into Fe by water gas (CO + H2). This reaction is known as vivification. This whole process is a continuous process.

ii. Bosch's process: in this process, water gas is mixed with steam and passed over heated catalytic mixture of Fe_2O_3 and Cr_2O_3 at 773K, then CO_2 and H_2 are obtained. The mixture is compressed and passed into water, CO_2 dissolves and H_2 is set free after that.

$C + H_2O \rightarrow CO + H_2$

$H_2 + CO + H_2O \rightarrow CO_2 + 2H_2O$

Properties:

1. Physical:

- Hydrogen is a lightest, colourless, odourless, and tasteless gas. It is sparingly soluble in water. It is inflammable and less reactive gas.

- It has a very low freezing and boiling point and due to low freezing point, liquid hydrogen is used as a cryogenic fluid (to produce low temperature).
- It must be transported under pressure in steel cylinders having almost negligible mass of gas.

2. **Chemical:**

- Reaction of hydrogen are slow at room temperature but rapid at high temperatures. It is neutral towards litmus, combustible and burns in air(O_2) with nearly invisible pale blue flame.

  $2H_2 + O_2 \rightarrow 2H_2O$
- When hydrogen is passed over heated metallic oxides, the latter is reduced to their respective metals.

  $CuO + H_2 \rightarrow Cu + H_2O$
- Group 1 and 2 (IA & IIA) are called highly electropositive metal. Whenever hydrogen reacts with these metals, they form ionic hydrides.

$2Na + H_2 \longrightarrow 2NaH$

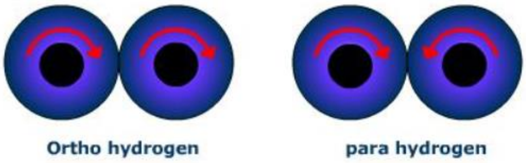
$CO + H_2 \longrightarrow CaH_2$

- When H_2 reacts with nitrogen, it gives ammonia (Haber's process).

  $N_2 + H_2 \xrightarrow{683K} 2NH_3$
- Hydrogenation of vegetable oil: when vegetable oils are exposed to air, the double bond in them gets oxidized and the oil becomes rancid (bad smell with taste). To avoid this vegetable oils are converted into edible fats (vanaspati ghee).

  Vegetable oils + $H_2 \xrightarrow{(Ni)}$ edible fats solid

Types of dihydrogen: A molecule of dihydrogen contains two atoms, in which the nuclei of both the atoms are spinning. Depending upon the direction of the spin of the nuclei, the hydrogens are of two types: ortho and para hydrogen:



- In ortho-hydrogen, the nuclear spins of the two hydrogen atoms are parallel. This means that the proton spins are aligned in the same direction.
- In para-hydrogen, the nuclear spins of the two hydrogen atoms are antiparallel. This means that the proton spins are aligned in opposite directions.
- Ortho and Para hydrogen resemble each other in their chemical properties but they do have different physical properties like thermal conductivity, boiling point due to difference in their overall spins.
- At room temperature the ratio of Para hydrogen to Ortho hydrogen is 1:3. This ratio is not exceeded even if we talk about high temperatures.
- Para hydrogen can be converted into Ortho hydrogen by using catalysts like platinum or iron, by mixing the paramagnetic molecules or by heating the sample to 800^0C or more.

Uses of hydrogen:

- In the form of an oxyacetylene flame, it is used in welding and cutting of metals at high temperatures of 2400^0C.
- It is used in the production of fuel gases like water gas, producer gas and coal gas. composition of water gas (CO-44%, H-48%, other gases-8%); producer gas (H-10%, CO-26%, N-55%).
- Liquid hydrogen can be used as a fuel for motor vehicles.
- It is used in the production of some important chemicals like ammonia, hydrochloric acid, and methanol.
- Hydrogenation of vegetable oil to form solid fats i.e. vanaspati ghee.
- Hydrogen is used to produce fuel oil and gasoline by the Bergius process.
- It is used in meteorological balloons to study weather conditions and it is used in manufacture of ammonia.

7.2 OXYGEN:

Oxygen, the element that sustains life on Earth, is a fundamental building block of nature. Represented by the symbol "O" and the atomic number 8 on the periodic table, it was discovered in the late 18th century by Carl Scheele and Joseph Priestley independently. Later, Antoine Lavoisier provided a comprehensive explanation of its role in combustion and respiration. Oxygen is a highly reactive, diatomic molecule, (O_2), in its elemental form.

Occurrence: Oxygen is the most abundant element in the Earth's crust, comprising nearly half of its mass (46%). It is also a significant component of the Earth's atmosphere, constituting about 21% of the air we breathe.

Position in periodic table: Oxygen belongs to Group 16 (VI A) of the periodic table, commonly referred to as the chalcogens. Oxygen is highly electronegative, meaning it has a strong tendency to attract electrons during chemical reactions. This property contributes to its ability to form stable compounds with various elements.

Preparation of oxygen: there are several methods of preparing oxygen-

1. By decomposition: compounds containing large amount of oxygen such as chlorates, nitrates, paramagnets etc, give oxygen on strong heating. It requires the temperature of about 600-750 K.

$2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$

2. By heating oxides: oxygen can be prepared by heating oxides of certain metals, low in electrochemical series.

$2HgO \longrightarrow 2Hg + O_2$

$2Ag_2O \longrightarrow 4Ag + O_2$

3. By electrolysis of water: Oxygen can be obtained by electrolysis of water containing a small amount of alkali or acid. Oxygen is collected at anode while hydrogen is liberated at cathode.

   $2H_2O(l) \rightarrow 2\ H_2(g) + O_2(g)$

4. Laboratory method: there are two methods of preparing O_2 in laboratory
   - Thermal decomposition of potassium chlorate: in this process oxygen is prepared by heating a mixture of potassium chlorate (4 parts) and manganese dioxide (1 part) in a hard glass tube to about 420K. the manganese dioxide acts as a catalyst here. In the absence of MnO_2, the decomposition takes place at 600^0C-750^0C. It also lowers the temperature for decomposition of $KClO_3$.

     $2KClO_3(s) \xrightarrow{MnO_2} 2KCl(s)+3O_2(g)$
   - Decomposition of hydrogen peroxide: H_2O_2 is readily decomposed into water and oxygen by catalyst such as MnO_2.

     $2H_2O_2(l) \xrightarrow{MnO_2} 2H_2O(l)+O_2(g)$

Properties:

1. **Physical:**
    - The gas is colourless, odourless, and tasteless gas at room temperature and pressure.
    - Oxygen is sparingly soluble in water, and its solubility increases at lower temperatures.
    - It forms oxides with every element except Nobel gases.
    - Molecular oxygen is paramagnetic in-spite of having even number of electrons.
2. **Chemical:**
    - It has no action on blue or red litmus.
    - On reacting with metals, it forms respective metal oxides. However less reactive metals (Ag, Au) do not combine with O_2.

      $4Na + O_2 \rightarrow 2Na_2O$

      $2Ca + O_2 \rightarrow 2CaO$

      $2Na + O_2 \xrightarrow{575K} Na_2O_2$ (sodium peroxide)
    - Oxygen supports combustion but itself is not combustible**.** Means it helps the fire burn more quickly.
    - It reacts with non-metals and forms their respective oxides.

      $N_2 + O_2 \rightarrow 2NO$

      $S + O_2 \rightarrow SO_2$

      $2C + O_2$(limited) → $2CO$

      $C + O_2$(excess) → CO_2
    - When oxygen reacts with compounds, it oxidises many compounds under specific condition.

      $4HCl + O_2 \xrightarrow{CuCL_2} 2Cl_2 + 2H_2O$ (reaction happens at 700K)
    - It oxidises ammonia to nitric oxide in presence of platinum gauze catalyst at 1073K:

      $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$
    - Hydrocarbons burn in excess O_2 to form CO_2 and water. These reactions are called combustion reactions and are highly exothermic in nature.

      $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ + heat

Uses of oxygen:

- Oxygen supports combustion. It is necessary for most combustion reactions, including those in vehicles, industries, and homes.
- It is used in the oxy-hydrogen or oxy-acetylene torches which are used for welding and cutting of metals.
- It is used in metallurgical process to remove the impurities by oxidation.
- Oxygen therapy is used in hospitals to treat patients with respiratory conditions. It is also used underwater during scuba diving and by mountaineers and pilots at high altitude.
- Liquid oxygen is used as rocket fuel, hydrazine in liquid oxygen provides the tremendous thrust in rockets.
- It is used as oxidizing agent and bleaching agent and used in making of steel.
- A mixture of liquid oxygen and carbon dust is used as explosive for coal mining.

7.3 NITROGEN:

Nitrogen, symbolized as N and with an atomic number of 7, is a vital element that plays a significant role in the natural world. Found abundantly in the Earth's atmosphere, nitrogen is an essential component of life. It was discovered in 18th century by Daniel Rutherford.

Occurrence: The most prevalent pure element on the planet is nitrogen. Despite this, it is not prevalent in the Earth's crust, accounting for only 19 ppm. Nitrogen molecules are mostly found in the air (78%) and it is found in the form of nitrates and nitrites in water and soil. The nitrogen cycle encompasses all of these elements, and they are all interrelated.

Position in periodic table: Nitrogen is the first element of Group 15 (V A) of the periodic table, which is also known as the nitrogen group. Group 15 elements are sometimes referred to as the pnictogens. Nitrogen is a non-metal and is found in nature primarily in the form of diatomic molecules (N_2).

Preparation of nitrogen:

1. Fractional distillation of liquid air: in this process air is reduced to liquid air by applying high pressure ranging between 100 and 200 atmospheres. This compressed air is then passed through fine jet where it undergoes expansion. This method is repeated several times which results in the formation of liquid air. The liquid formed, undergoes fractional distillation. The boiling point of nitrogen (-196^0C) is lower than that of the liquid oxygen (-183^0C) and hence it distils out, leaving behind liquid oxygen. Nitrogen is obtained from the impure liquid.
2. Laboratory method: Nitrogen is prepared in the laboratory by heating an equimolar aqueous solution of ammonium chloride and sodium nitrite. This is heated and small amounts of water are added to this reaction. The ammonium nitrite formed as result of double decomposition reaction, decomposes to form nitrogen.

$NH_4Cl + NaNO_2 \rightarrow NH_4NO_2 + NaCl$

$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

3. Ammonia decomposition: Ammonia (NH_3) can be decomposed into nitrogen and hydrogen gases. This method involves passing ammonia gas over a catalyst at high temperatures, typically around 500-700 degree Celsius (932-1292 degrees Fahrenheit). The reaction is as follows:

   $2NH_3(g) \xrightarrow{\Delta} 3H_2(g) + N_2(g)$

4. Nitrogen can also be prepared by passing ammonia gas over hot, reduced metal or metal oxide surfaces. The metal catalyst reacts with ammonia to produce nitrogen gas. This method is often used in industrial processes.

Properties:

1. **Physical:**
   - Nitrogen is a colourless, odourless gas that can also be used as a liquid. The element is found in the form of dinitrogen (N_2).
   - Nitrogen is a diatomic gas at room temperature and standard pressure.
   - It is sparingly soluble in water.

- Nitrogen undergoes condensation to form a colourless liquid which on solidification results in the formation of snow like mass.

2. **Chemical:**
   - Dinitrogen has a high bond enthalpy due to the N=N bond. Due to this it is inert at room temperature. The reactivity increases as the temperature increases.
   - At high temperatures, nitrogen molecules react with metals to form respective ionic nitrides and with non-metals to form covalent nitrides.
   - At about 600-700 K it reacts with hydrogen to form ammonia in Haber's Process.

     $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
   - Nitric oxide is formed when nitrogen molecule reacts with oxygen molecule at a very high temperature.

     $N_2(g) + O_2(g) \overset{heat}{\longleftrightarrow} 2NO(g)$
   - Some oxides of nitrogen are neutral oxides, as they do not react with either acid or base and they do not have the tendency to form salts when they are reacted with acids or bases. For example- NO and N_2O (nitrous oxide) do not display any basic or acidic characteristics. On the contrary, oxides like NO_2, and N_2O_3 are considered as acidic oxide because they tend to form acidic solution on reaction with water. N_2O_5 is a basic oxide because it forms basic solution on reacting with water.

Uses of nitrogen:

- Nitrogen is often used to create inert atmospheres in applications where oxygen might react with sensitive materials. For example, it is used in the production of electronic components, metal heat treatment, and in the preservation of perishable goods.
- Nitrogen is used in the food industry for packaging products to extend shelf life. Liquid nitrogen is also used in the food industry for freezing and cryogenic grinding.
- Some construction equipment makes use of compressed nitrogen gas to assist the hydraulic system in providing more power to devices like hydraulic hammers. The breakdown of Sodium Azide produces nitrogen gas, which is used to inflate airbags.
- Nitrogen is used in the chemical industry as a blanketing gas to prevent unwanted reactions with oxygen and moisture. It is also used in the production of ammonia, which is a key component of fertilizers.
- Liquid nitrogen is used in cryopreservation (sperms and eggs) and cryosurgery.
- Nitrogen is used to fill tires, especially in vehicles where stable tire pressure is crucial, such as aircraft and racing cars.
- Nitrogen is used in enhanced oil recovery techniques where it is injected into oil wells to increase pressure and aid in the extraction of oil.
- Nitrogen is used for pressure testing and leak detection in air conditioning and refrigeration systems. It helps ensure that these systems are free of leaks and operate efficiently.

Exercise 1

1. Isotopes of hydrogen differs in [CGPSC ACF 2017]
   (a) No. of neutrons in nucleus of isotopes
   (b) No. of protons in the nucleus of isotopes
   (c) No. of electron in the isotopes
   (d) No. of proton and neutron are same in all isotopes
   (e) None of these
2. Which of the following oxide of nitrogen is **not** acidic? [Raj ACF 2018]
   (a) N_2O
   (b) N_2O_3
   (c) NO_2
   (d) N_2O_5
3. Which isotope of Hydrogen does not have neutrons in the nucleus [MPPSC SFM 2018]
   (a) $1H^1$
   (b) $1D^2$
   (c) $1T^3$
   (d) None of these
4. Ortho and para hydrogens have [MPPSC SFM 2018]
   (a) Same physical properties but different chemical properties
   (b) Different physical properties but same chemical properties
   (c) Same physical and chemical properties
   (d) Different physical and chemical; properties
5. Haber's process is used for the manufacturing of [MPPSC SFS Main 2019]
   (a) O_2
   (b) N_2
   (c) H_2
   (d) NH_3
6. Number of isotopes of Hydrogen is [MPPSC SFS Main 2019]
   (a) 1
   (b) 2
   (c) 3
   (d) 4
7. Hydrogen gas is used in [MPPSC SFS Main 2021]
   (a) Preparation of ammonia
   (b) Preparation of hydrochloric acid
   (c) Preparation of methanol
   (d) All of the above

(1.) a, (2.) a, (3) a, (4) b, (5) d, (6) c, (7) d

7.4 ALCOHOL AND ACETIC ACID:

Alcohol: hydroxyl derivatives of alkane is known as Alcohol. Alcohols are compounds which contain one or more hydroxyl (-OH) groups directly attached to a carbon chain. Alcohols in the free-form are not a common occurrence in nature; they are found mainly in the essential or volatile oils obtained from flowers, leaves, and stems of the plants.

C_nH_{2n+2} (alkane) $\xrightarrow{+OH}$ $C_nH_{2n+1}OH$ (alcohol)

There are many types of alcohol like mono-hydric, dihydric etc. here are two most common types of them:

1. **Methanol or methyl alcohol**: it is a monohydric type of alcohol with the formula CH_3OH. It is also known as wood alcohol or methyl alcohol. It has a distinctive odour which is milder and sweeter than ethanol. Consumption of methanol is toxic and can cause blindness.

   Preparation: Carbon monoxide and hydrogen react over a catalyst to produce methanol. Today, the most widely used catalyst is a mixture of copper and zinc oxides, supported on alumina.

   $CO + 2H_2 \rightarrow CH_3OH$

   Properties:

   - It is a flammable, light, poisonous liquid.
   - It is soluble in both water and organic solvents.
   - It has a slightly sweet odour.
   - Methanol (IUPAC name) is highly flammable and burns with a colourless, non-luminous flame.
   - On reaction with acetic acid, it gives ester.

   Uses:

   - Methanol is used as a solvent,antifreeze,and fuel in industrial processes.It is also a feedstock for production of chemicals like formaldehyde and acetic acid.
   - Methanol can be used as an alternative fuel source,either directly in methanol fuel cells or indirectly as a feedstock for biodiesel production

Note: Denatured alcohol: denatured alcohol also called methylated spirit. It is mixture of 10% methanol and 90% ethanol. It is used as a solvent, paints, in varnish industry and as a fuel. It is not considered to be fit for drinking.

2. Ethanol or ethyl alcohol: it is also a monohydric type of alcohol with the formula C2H5OH.It is called grain/drinking alcohol

   Preparation:

   a) The most common method of ethanol (IUPAC name) production is fermentation process. Fermentation is the process of culturing yeast under favourable thermal conditions to produce alcohol. It is a

   b) biological process and because yeasts perform this conversion in the absence of oxygen, alcoholic fermentation is considered an anaerobic process.

   - Fermentation: It starts with cleaning and washing of raw corn to remove dirt and other impurities. The raw material is crushed and heated in warm water to extract its starch content. The material is transferred to a fermentation tank where it is mixed with yeast. the tank is then arranged in a warm, dark place (around 30°C -35°C) and let the fermentation proceed. This may take several days. During this process, Enzymes (from yeast) convert the complex starch molecules into maltose that in further biochemical steps converted into simple glucose units. Yeast, then converts sugar (like maltose, su crose, fructose) into ethanol and carbon dioxide through fermentation.

$$C12H22O11\ (maltose) + H2O \xrightarrow{Maltase} 2C6H12O6\ (glucose)$$

$$C6H12O6 \xrightarrow{Invertase} 2C2H5OH + 2CO_2$$

- Distillation: The fermented material, known as mash, is further processed using one single step distillation to separate liquid from solid. The liquid is impure and contains only 8-12% ethanol. Ethanol has a lower boiling point than water (78.37°C),so it will vaporize first on heating. The distillation of liquid increases the purity level of ethanol and the final product is 96% ethanol.

c) From alkane: Ethanol is made by hydration of ethene (CH2=CH2).This is the easiest and most cost-effective method to manufacture ethanol.The reaction is carried out in the presence of phosphoric acid (H3PO4) used as a catalyst. The mixture is heated to 3000C and the gases react over the catalyst to form ethanol. The gaseous mixture of unreacted ethene and product ethanol is cooled down which liquefies ethanol.

$$C2H4 + H2O \xrightarrow{H_3PO_4} C2H5OH$$

d) From alkyl halide: ethanol can be prepared by hydrolysis of ethyl chloride (or bromide) with aqueous potassium (or sodium) hydroxide.

$C2H5Cl \xrightarrow{KOH(aq)} C2H5OH$ + KCl

$C_2H_5Br + NaOH_{(aq)} \rightarrow C_2H_5OH + NaBr$

e) From Grignard reagent: The preparation of ethanol using a Grignard reagent involves a two-step process: the formation of the Grignard reagent (CH_3CH_2MgBr) and its subsequent reaction with a suitable electrophile. The Grignard reagent is typically formed by reacting an alkyl or aryl halide with magnesium in an ether solvent.

Grignard reagent: it is an organo-magnesium compound with the general formula R-Mg-X, where R refers to alkyl or aryl group and X refers to a halogen.

$CH_3CH_2MgBr + HCHO \rightarrow CH_3CH_2OH + MgBrOH$

Properties:

- It is a clear, colourless liquid with a characteristic odour and a slightly sweet taste.
- It has a boiling point of 78.37^0C and a melting point of -114.1^0C.
- Ethanol is highly soluble in water and most organic solvents. Due to the presence of bond between electronegative atom oxygen and hydrogen, the O-H bond acquires polarity. Hence, because of polarity in O-H bond, it forms a hydrogen bond with water, which is responsible for the solubility of ethanol in water.
- On litmus paper it shows neutral behaviour and it is highly flammable.
- Ethanol is oxidized to acetic acid with alkaline $KMnO_4$ or acidified $K_2Cr_2O_7$. During this reaction, the orange colour of $K_2Cr_2O_7$ changes to green. Therefore, this reaction can be used for the identification of alcohols.

  $3C_2H_5OH + 2K_2Cr_2O_7 + 8H_2SO_4 \xrightarrow{[O]} 3CH_3COOH + 4Cr_2(SO_4)_3 + 2K_2SO_4 + 11H_2O$
- When vapour of ethanol is passed over heated copper catalyst at 573K, it is dehydrogenated to acetaldehyde.

  $C_2H_5OH \xrightarrow{Cu} CH_3CHO + H_2$
- Ethanol when heated with excess concentrated sulphuric acid at 443K, it undergoes dehydration to give ethene (in intramolecular) and diethyl ether (in intermolecular).

Uses: Some of the common uses of ethanol include:

- Ethanol is the active ingredient in alcoholic beverages such as beer, wine, and spirits. It is consumed recreationally in moderate quantities.
- Ethanol is used as a biofuel additive in gasoline. Ethanol-blended fuels, such as E10 (10% ethanol and 90% gasoline), are used in many countries to reduce greenhouse gas emissions and dependence on fossil fuels.
- Ethanol is a polar solvent and is used in the pharmaceutical, cosmetic, and chemical industries for dissolving various substances. It is an essential component in the production of perfumes, lotions, and personal care products.
- Ethanol is used as an antiseptic to disinfect skin and surfaces. It is used as a common ingredient in hand sanitizers and disinfectant sprays as well.
- Ethanol is used as a preservative in pharmaceuticals, cosmetics, and food products. It is also used in the food and beverage industry as a flavouring agent and as a solvent for food extracts.
- Ethanol is sometimes added to windshield washer fluids and de-icing products to prevent them from freezing at low temperatures.
- It serves as a raw material or intermediate in the production of other chemicals, such as ethyl acetate, acetic acid, and ethylene.

Acetic acid: Acetic acid, also known as Ethanoic acid (IUPAC name), is a key chemical compound used in various industrial and laboratory applications. It is a carboxylic acid consisting of a methyl group that is attached to a carboxyl functional group with the chemical formula CH_3COOH.

Preparation:

a) Acetic acid is produced industrially via the carbonylation of methanol. In this Reaction, a methyl iodide intermediate is created between methanol and hydrogen iodide. After reacting this intermediate with carbon monoxide and treating the resulting chemical with water, the acetic acid product is generated.

CH_3OH (methanol) + HI (hydrogen iodide) → CH_3I (methyl iodide intermediate) + H_2O

CH_3I + CO (carbon monoxide) → CH_3COI (acetyl iodide)

$CH_3COI + H_2O \rightarrow CH_3COOH$ (acetic acid) + HI

b) Another method of preparation of acetic acid is by Quick-Vinegar process. In this process, a dilute aqueous solution of ethyl alcohol is oxidized in presence of enzyme Myco-derma Aceti.

$$C_2H_5OH + O_2 \xrightarrow{mycoderma} CH_3COOH + H_2O$$

c) Acetic acid can be obtained by oxidation of acetaldehyde. Some naphthalene salts of cobalt, chromium (potassium dichromate), and manganese with sulphuric acid can be employed as metal catalyst in this process.

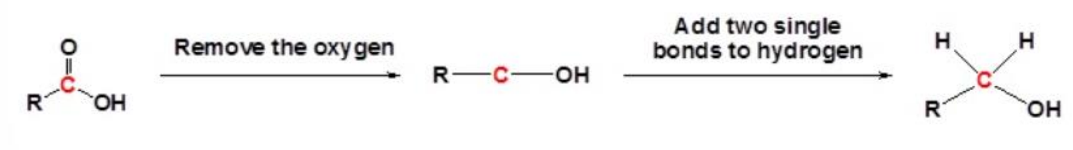
$$2CH_3CO + O_2 \xrightarrow{K2Cr2O7} 2CH_3COOH$$

Properties:

- At STP, the melting and boiling points of ethanoic acid are 16^0C and 118^0C respectively.
- Acetic acid tastes sour and has a strong vinegar smell.
- the conjugate base of acetic acid is acetate, given by CH_3COO^-.
- Even though ethanoic acid is considered as a weak acid, in its concentrated form, it possesses strong corrosive powers and can even damage the human skin if exposed to it.

- Acetic acid is sparingly soluble with water, alcohol, ether, and most organic solvents.
- It turns blue litmus paper into red.
- Carboxylic acids can be converted to alcohols using lithium-aluminium hydride ($LiAlH_4$). An aldehyde is produced as an intermediate during this reaction, but it can not be isolated because it is more reactive.

$$RCOOH \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} RCH_2OH$$



- On reacting with chlorine in presence of red phosphorus, it forms trichloroacetic acid.

$$CH_3COOH + Cl_2 \xrightarrow{red\ phosphorus} CH_3COOCl$$

- Acetic acid can undergo various chemical reactions, including Esterification, where it reacts with alcohols to form esters and water.

$CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5$ (ester) + H_2O

- It can react with bases to form acetate salts and water.

$NaOH + CH_3COOH \rightarrow CH_3COONa$ (sodium acetate) + H_2O

Note: when an acid having α-hydrogen atoms reacts with a halogen in the presence of red phosphorous, it results in the chlorination of α-carbon to produce 2-chlorothanoic acid. This reaction is known as Hell-Volhard-Zelinsky reaction-

$R\text{-}COOH + Cl_2 + P \rightarrow R\text{-}COCl + HCl$

- On reacting with sodium carbonate/bicarbonate, it gives salt, water, and carbon dioxide.

$2CH_3COOH + Na_2CO_3 \rightarrow 2CH_3COONa + H_2O + CO_2$

Uses of acetic acid:

- Acetic acid is widely used in the production of vinegar, which is a dilute solution of acetic acid in water and contains 5-20% acetic acid by volume.
- It is used as a solvent in the production of various plastics and chemicals. Like acetone, esters, perfumes etc.
- Acetic acid is employed in the manufacture of synthetic fibres, fabrics, and food additives, pickling culture, and condiments (ketchup, mayonnaise).
- It is also utilized in the production of pharmaceuticals, dyes, and insecticides.
- The manufacture of rubber involves the use of ethanoic acid. It is also widely used in the production of VAM (vinyl acetate monomer).
- Medically, acetic acid has been employed to treat cancer by its direct injection into the tumour.
- Acetic acid is used as an antiseptic due to its antibacterial qualities.

Exercise 2

1. Methylated spirit contains [CG pariyojna 2021]
   (a) 2% to 5% methanol
   (b) 5% to 7% methanol
   (c) 10% to 15% methanol
   (d) 40% to 50% methanol
2. Acetic acid is obtained when [CGPSC ACF 2020]
   (a) Acetaldehyde is oxidised with potassium dichromate and sulphuric acid
   (b) Methyl alcohol is oxidised with potassium dichromate
   (c) Calcium acetate is distilled in presence of calcium formate
   (d) Glycerol is heated with sulphuric acid
3. In presence of catalyst (phosphorus), chlorine reacts with acetic acid to form [CGPSC ACF 2020]
   (a) $CH_3 - C - CL_2 - OH$
   (b) $CH_3 - C = O - Cl$
   (c) $CH_3 - C = O - OCl$
   (d) None of these
4. When CH_3MgBr (Grignard reagent) is made to react with formaldehyde and product is hydrolysed, then which of the following compound is obtained [MPPSC SFM 2018]
   (a) CH_3CH_2OH
   (b) CH_3OH
   (c) CH_3COOH
   (d) CH_3CHO
5. Which of the following product is correct in the given reaction? [MPPSC SFM SP 2019]

   $$RCOOH \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} ?$$

   (a) RCH_2OH
   (b) R_2CH_2OH
   (c) R_3CH_2OH
   (d) RCH_3OH
6. What is the IUPAC name of acetic acid? [MPPSC SFM SP 2019]
   (a) Methanoic acid
   (b) Propenoic acid
   (c) Ethanoic acid
   (d) All of the above
7. Ethyl alcohol is soluble in water because it [MPPSC SFS Main 2019]
   (a) Forms hydrogen bonds with water
   (b) Ionised in water
   (c) Shows isomerization in water
   (d) Shows resonance in water

(1.) c, (2.) a, (3) c, (4) a, (5) a, (6) c, (7) a

CHAPTER

8

POLYMERS, SOAPS & DETERGENTS

Syllabus: introduction, rubber, nylon, polythene, Teflon, PVC, Bakelite, biodegradable polymer, resin; soaps & detergents.

8.1 INTRODUCTION

The term polymer is used to describe a very large molecule that is made up of many repeating small molecular units. These small units are called monomers and the chemical reaction that combines the monomers together is called polymerization. The term 'polymer' is a Greek term which means- Polus (many) and Meros (part). This term was coined by Berzelius.

Homopolymers and Copolymers: polymers which are formed by only one type of monomer are called homopolymers. Some examples are as follows:

Homopolymer	Monomer
Starch	Glucose
Cellulose	Glucose
Polyethylene	Ethylene
Polyvinyl chloride	Vinyl chloride
Teflon	Tetrafluoro ethylene
Nylon-6	Caprolactam

Polymers which are formed by more than one type of monomers are known as copolymers. For ex.

Copolymer	Monomer
Saran	Vinyl chloride & vinylidene chloride
SAN	Styrene & acrylonitrile
ABS	Acrylonitrile, butadiene & styrene
Butyl rubber	Isobutylene & isoprene
Buna-S	Styrene & butadiene
Buna-N	Acrylonitrile & butadiene
Nylone-66	Hexamethylenediamine & adipic acid
Terylene	Terephthalic acid ethylene glycol

Classification of polymers: polymers are classified in following ways:

1. **Classification based upon source:**

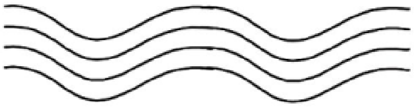
   1.1. **Natural polymers:** polymers which are obtained from animals and plants as natural polymers. They are generally monodispersed, so there PDI (poly dispersity index) is 1. For ex.

Natural polymer	**monomers**
Polysaccharide	Monosaccharide
Proteins	α-L-amino acid
Nucleic acid	Nucleotide
Silk	Amino-acid
Natural rubber	Isoprene (2-methyl-1,3-butadiene)
Gutta-percha	Isoprene

   1.2. **Semisynthetic polymers:** Polymers which are prepared from natural polymers are known as semisynthetic polymers. Most of them are prepared from cellulose. Examples are- cellulose acetate, cellulose nitrate, cellulose xanthate, and rayon.

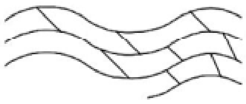
   1.3. **Synthetic polymers:** man-made polymers, i.e. polymers prepared in laboratory are known as synthetic polymers. Since these polymers are always poly-dispersed, there PDI is greater than 1. Examples are- PVC, polyethylene, nylon-6, nylon-66, terylene, synthetic rubber etc.

2. **Classification based upon shape:**



   2.1. **Linear polymers:** polymers whose structure is linear is known as linear polymer. The various linear polymeric chains are stacked over one another to give a well packed structure. The chains are highly ordered with respect to one another. The structure is close packed in nature, due to which they have high densities, high melting point and high tensile strength. They can be converted into fibers. In other word all fibers are linear polymers. Ex. Cellulose, silk, nylon (6 & 66), terylene, nucleic acid, polyethylene, PVC, polystyrene, and polyamides.

   2.2. **Branched chain polymers:** polymers whose monomeric units constitute a branched chain. Due to the presence of branches, these do not pack well. As a result, branched chain polymers have lower melting points, low densities, and tensile strength as well. Ex. Amylopectin, glycogen, all vulcanized rubbers, low density polyethylene.



   2.3. **Cross-linked/3-d network polymers:** in these polymers the initially forms linear polymeric chains are joined together to form a three-dimensional network structure. These are hard, rigid, and brittle. They are always condensation polymers. Ex. Resins, Bakelite, Melamine, Glyptal etc.

3. **Classification based upon synthesis:**

3.1. **Condensation polymers:** polymers that are formed by the combination of monomers with the elimination of simple molecules such as water or alcohol. this process is called condensation polymerization. Proteins, starch, cellulose etc are the example of natural condensation polymers. Two main synthetic polymers of condensation types are polyesters (Terylene or Dacron) and poly amides (Nylon-66), proteins, Bakelite.

3.2. **Addition polymers:** These polymers are formed by the addition of the molecules of the monomers to form a large molecule without elimination of anything. The process of the formation of addition polymers is called addition polymerisation. For ex.

n[$CH_2=CH_2$] (ethene) $\xrightarrow{Polymerisation}$ [-CH_2-CH_2-]$_n$ (polythene)

Note: Ziegler-Natta polymerization: addition polymerization which takes place in the presence of Zieglar-Natta catalyst [$(C_2H_5)_3Al$] and [$TiCl_4$] is called as Ziegler-Natta polymerization or coordination polymerization. This reaction always gives linear, stereo-regular polymers and due to this, they allow the synthesis of stronger and stiffer polymers. These polymers have great resistance to cracking and heat. High density polyethylene is prepared by this catalyst.

4. **Classification based on intermolecular forces:** On basis of magnitude of secondary (intermolecular) force, following are some categories:

4.1. **Elastomers:** These are the polymers having very weak intermolecular forces of attraction between polymer chains. It has the elastic nature and has a very weak Van-der-wall force. Elastomers have an ability to stretch out over ten times their normal length. For ex. Vulcanized rubber.

4.2. **Fibers:** These are the polymers which have bit strong intermolecular forces such as hydrogen bonding and the polymeric chains are highly ordered with respect to one another.

Due to these forces, fibers have high tensile strength, least elasticity, high melting power and low solubility. For ex. Cellulose, nylon, terylene (Dacron, Teron, Cronar, Mylar), wool, silk.

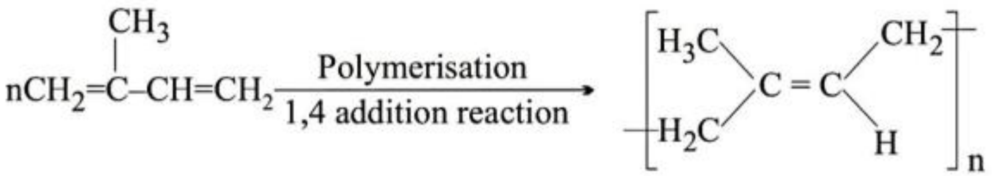
4.3. **Thermoplastic:** thermoplastic polymers are polymers that have both ordered crystalline regions and amorphous non-crystalline regions as well. The intermolecular forces are in between elastomers and fibers as there are no cross-links between the polymeric chains. They are hard at room temperature, become soft and viscus when heated upon and become rigid again on cooling. This process of heating and cooling can be repeated as many times as desired without any change in properties. As a result, these plastics used for making toys, buckets, telephone and tv cases etc. some examples are- polyethene, polypropylene, polystyrene, PVC, Teflon, PCTFE etc.

Note: addition polymers obtained from ethylene and ethylene derivatives are thermoplastic polymers.

4.4. **Thermosetting:** polymers which becomes hard on heating are called thermosetting polymers. They can be heated once, when it permanently sets into a solid, which cannot be remelted by heating. Thermosetting are cross-linked polymers. Greater the degree of cross-linking that exist, the more rigid is the polymer. This cross-linking reduces the mobility and causing them to be relatively brittle material. They are condensation polymers. For ex. Bakelite, melamine, phenol formaldehyde resin, urea-formaldehyde resin, etc.

8.2 RUBBER

i. **Natural Rubber:** natural rubber is obtained from nearly five hundred different plants but the main source is a plant namely Hevea Brasiliensis. It is obtained in the form of milky sap known as latex. This latex is coagulated with acetic acid and formic acid. The raw natural rubber is a soft gummy and sticky mass. It is insoluble in water, dilute acids, and alkalis but soluble in non-polar solvents. Natural rubber is a polymer of 2-methyl-1, 3-butadiene (isoprene-C_5H_8). All the double bonds in rubber are cis, hence natural rubber is cis-polyisoprene. Early notable works on rubber were done by Joseph Priestley. Gutta-percha is a naturally occurring isomer of rubber which is trans-polyisoprene:

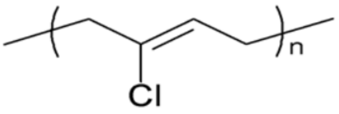


[Isoprene] [gutta percha]

- **Vulcanization:** in-order to give strength and elasticity to natural rubber, it is vulcanized. Heating of rubber with sulfur at 150^{0}C for few hours is known as vulcanization. The sulfur acts as a cross-linking agent and after vulcanization, rubber gets cross-linked and becomes hard. This process can be enhanced in the presence of certain organic compounds known as accelerators. This process is discovered by Charles Goodyear in late 19th century.

  Natural rubber is used for making shoes, water-proof coats, and golf balls. Vulcanized rubber is used for manufacture of rubber bands, gloves tubing and car tyers.

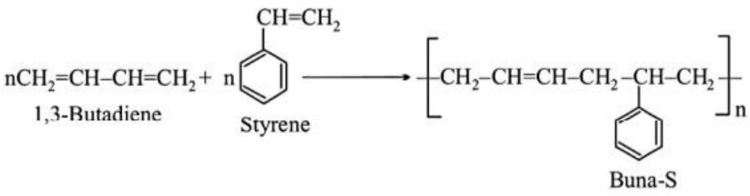
ii. **Synthetic rubbers:** Synthetic rubbers are produced from petroleum and natural gas. It is obtained by polymerization of 1, 3 – butadiene derivatives or by copolymerization of 1,3 – butadiene along with an unsaturated monomer. They have some improved properties like flexibility, toughness, and more durability than natural rubber. Some examples are-



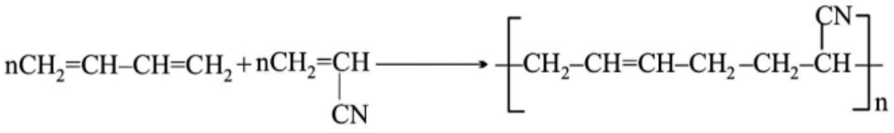
Neoprene

- **Neoprene:** It is made by polymerisation of 2-chloro-1,3-butadiene, it is commonly known as chloroprene. Neoprene is commonly used to mass-produce reliable gaskets, cable jackets, tubing, seals, tire-sidewalls, gasoline hoses, wetsuits, and orthopaedic braces.

- **Buna-N:** It is a copolymer of 1, 3 – butadiene and acrylonitrile, it is formed in the presence of a peroxide catalyst. It is very resistant to action of petrol, lubricating oil and many organic solvents. It is mainly used for making fuel tanks.



- **Buna-S:** it is a copolymer of 3 moles of butadiene and one mole of styrene. It is an elastomer (general purpose styrene rubber/GRS). It is extremely resistant to wear & tear, therefore used in manufacture of tyres and other mechanical rubber goods.

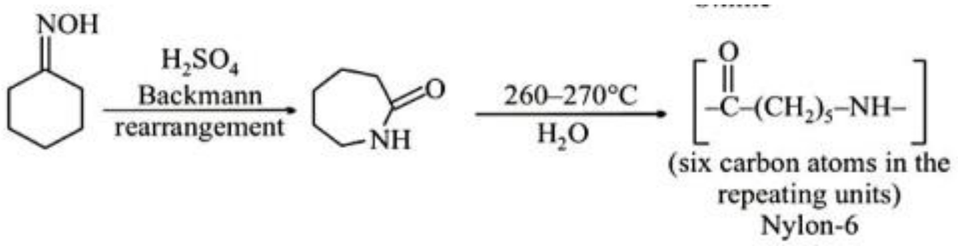


$$nCH_2{=}CH{-}CH{=}CH_2 + nCH_2{=}\underset{\displaystyle CN}{\underset{|}{C}H} \longrightarrow \left[CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\overset{\displaystyle CN}{\overset{|}{C}H} \right]_n$$

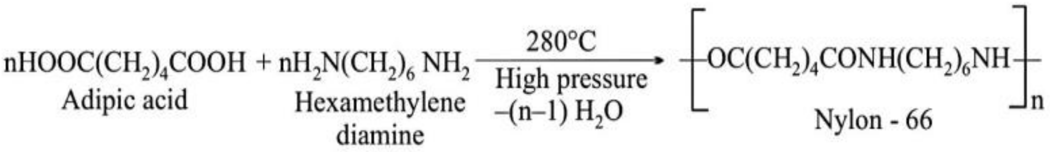
8.3 NYLON

Nylon is used as a general name for all synthetic fibres forming polyamides, i.e. having protein like structure. A number is usually suffixed with its name which refers to the number of carbon atoms present in the monomers. For ex. Nylon-6, nylon-66.

i. Nylon-6: it is prepared by prolonged heating of caprolactam at 260^0-270^0C. It is formed by self-condensation of molecules of amino caproic acid. Caprolactam is obtained by Backmann rearrangement. It is also known as Perlon-L. It is used for making radiator grills, stadium seats, and firearm components.



ii. Nylon-66: it is obtained by polymerization of hexamethylenediamine (diamine with 6 carbon atoms) and adipic acid. It is used for making products like battery modules, luggage, conveyor belts, and friction bearings.



$$\underset{\text{Adipic acid}}{nHOOC(CH_2)_4COOH} + \underset{\text{Hexamethylene diamine}}{nH_2N(CH_2)_6\,NH_2} \xrightarrow[\text{High pressure } -(n-1)\,H_2O]{280°C} \underset{\text{Nylon - 66}}{\left[OC(CH_2)_4CONH(CH_2)_6NH \right]_n}$$

8.4 POLYETHYLENE

Polyethylene, also known as polythene or polyethene is one of the mostly used plastics in the world. Polyethylene usually has a linear structure and are known to be addition polymers. The primary application of these synthetic polymers is in packaging. The general formula of polyethylene can be written as $(C_2H_4)_n$. Most types of polyethylene are thermoplastic However, some modified polyethylene plastics exhibit thermosetting properties as well. An example of such a class of polyethylene is cross-linked polyethylene (often abbreviated as PEX). It was first synthesized by Hans von Pechmann in 1898, later in the 20th century Eric Fawcett and Reginald Gibson accidently discovered this. It has two types and both are thermoplastics.

a) **Low density polyethylene (LDPE):** it is manufactured by heating ethylene at 200^{0}C under a pressure of 1500 atm and in the presence of traces of oxygen. This polymerization is a free radical polymerisation. It consists of highly branched chain molecules. The branching does not allow the polymer molecules to undergo close packing. It is a transparent polymer of moderate tensile strength, high toughness, and low melting point (110^{0}C). it is widely used as a packing material and as insulation for electrical wires and cables.

$nCH_2=CH_2 \xrightarrow{200^0C} [-CH_2-CH_2-]_n$

b) **High density polyethylene (HDPE):** it is prepared with the use of Zieglar-Natta catalyst at 160^{0}C under pressure of 6 to 7 atm. It has a higher melting point (130^{0}C) than LDPE but has a very low melting point when compared to other materials. It consists of closely packed linear molecules and has greater toughness, hardness, and tensile strength than LDPE. It is used in the manufacture of containers (buckets, tubes), house wares, bottles, and toys.

8.5 TEFLON

Teflon, also known as polytetrafluoroethylene (PTFE), is a synthetic fluoropolymer of tetrafluoroethylene. Discovered by Dr Roy Plunkett in 1938, Teflon has become synonymous with non-stick coatings and is renowned for its unique properties and wide-ranging applications in various industries. The monomer used in preparation of Teflon is tetrafluoro ethylene ($CF_2=CF_2$), which is a gas at room temperature. This is polymerized by using free-radical initiators such as hydrogen peroxide or ammonium persulphate at high pressure to produce poly tetrafluoro ethylene (Teflon).

$n\,(CF_2= CF_2) \xrightarrow{Polymerization} [-CF_2-CF_2-]_n$ (Teflon)

Properties:

- One of Teflon's most well-known properties is its excellent non-stick surface. This quality makes it ideal for coating cookware, preventing food from sticking during cooking and simplifying the cleaning process.
- Teflon is highly resistant to chemical reactions, making it resistant to acids, bases, and many organic solvents.
- Teflon can withstand high temperatures without undergoing significant degradation. It remains stable at temperatures ranging from (-200°C to 260°C).
- Teflon has a low coefficient of friction, which means it reduces friction and wear when used as a coating on various surfaces.
- Teflon is flexible even at low temperatures.

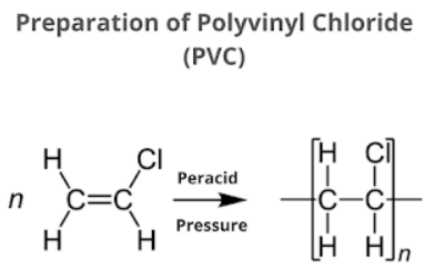
Uses:

- Teflon-coated pans and pots are popular in households and professional kitchens, ensuring easy food release and effortless cleaning.
- Teflon is used in industrial settings for lining tanks and pipes, manufacturing gaskets, and providing a non-stick surface for conveyor belts.
- Teflon is employed in the production of insulated wires, cables, and connectors due to its excellent electrical insulation properties.
- Teflon is utilized in the manufacturing of components such as seals, gaskets, and bearings, enhancing the efficiency and longevity of automotive parts.

- Teflon coatings are applied to medical devices and instruments due to their biocompatibility and non-reactive nature.
- Teflon is used in aerospace applications for its low friction properties, and Teflon coatings are applied to fabrics to make them resistant to stains and water, creating durable and easy-to-clean textiles.

8.6 POLYVINYL CHLORIDE

Polyvinyl Chloride, commonly known as PVC, is a versatile synthetic polymer with a wide range of applications due to its unique properties. Its exceptional characteristics and affordability have made it one of the most widely used plastics globally. It was synthesized in the year 1872 by Eugen Baumann. Later in the 20th century PVC was commercially used by Ivan Ostro and Fritz Klatte.


Preparation of Polyvinyl Chloride (PVC)

It is prepared by radical polymerization of vinyl chloride to produce material composed of an average of 10,000 to 24,000 monomer units. The monomer vinyl chloride is treated with peracid under pressure to obtain Polyvinyl Chloride (PVC).

Properties:

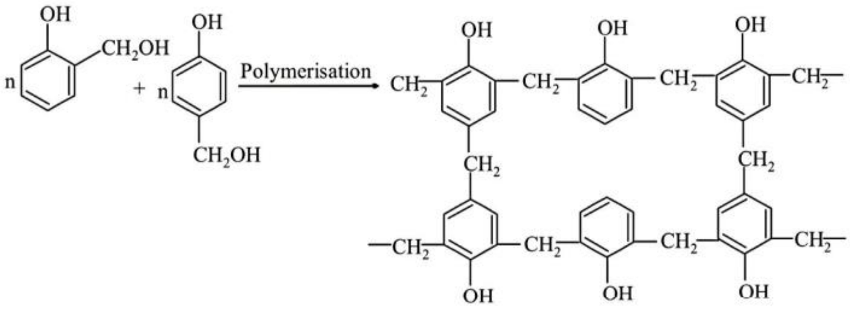
- PVC is a highly durable material that can withstand harsh weather conditions, chemicals, and abrasion.
- PVC can be rigid or flexible, depending on the additives used during its production.
- PVC has inherent fire-resistant properties, making it a preferred choice for electrical insulation and construction materials, where fire safety is essential.
- PVC is resistant to many chemicals, acids, and alkalis and it is an excellent electrical insulator.
- It is insoluble in all hydrocarbon solvents, except some chlorinated solvents.

Uses:

- PVC is widely used in the construction industry for pipes, fittings, window frames, doors, and roofing membranes.
- PVC is used for electrical insulation on wires and cables due to its excellent insulating properties. It is also used in the production of electrical conduits and cable insulation.
- PVC is utilized in medical devices such as tubing, blood bags, and IV bags.
- It is found in car interiors, wiring harnesses, and under-the-hood applications and it is used in blister packaging, shrink wrap, and food packaging films.
- Flexible PVC is used in the fashion industry for raincoats, boots, and inflatable structures.
- PVC sheets are commonly used for signs, banners, and displays and PVC pipes are widely used for water supply, drainage, and sewage systems.

8.7 BAKELITE

Bakelite was one of the first synthetic plastics ever created. Developed by Belgian chemist Leo Baekeland in the early 20th century, Bakelite revolutionized various industries due to its unique properties and versatility. Initial methods of preparing Bakelite involved the heating of formaldehyde and phenol in the presence of one of the following catalysts -zinc chloride ($ZnCl_2$), hydrochloric acid (HCl), or ammonia (NH_3).



Cross - linked polymer (Bakelite)

Properties:

- Bakelite is an excellent electrical insulator.
- Bakelite is highly heat-resistant, allowing it to withstand high temperatures without deforming or losing its structural integrity.
- Bakelite is resistant to many chemicals, including acids and bases.
- Bakelite is a thermosetting plastic, meaning that it hardens irreversibly when heated. Once it is moulded and set, it cannot be melted or reshaped.
- Bakelite is a hard and tough material, providing durability and impact resistance.

Uses:

- Bakelite was widely used in the early 20th century for electrical insulators and components like switches, plugs, sockets, and other electrical devices.
- Bakelite found applications in various industrial settings, such as in the manufacturing of gears, bearings, and other mechanical components.
- Bakelite was used in the automotive industry for manufacturing parts like distributor caps, brake cylinders etc.
- Bakelite was popular in the production of consumer goods, including jewellery, kitchenware, and various decorative items.

8.8 BIODEGRADABLE POLYMER

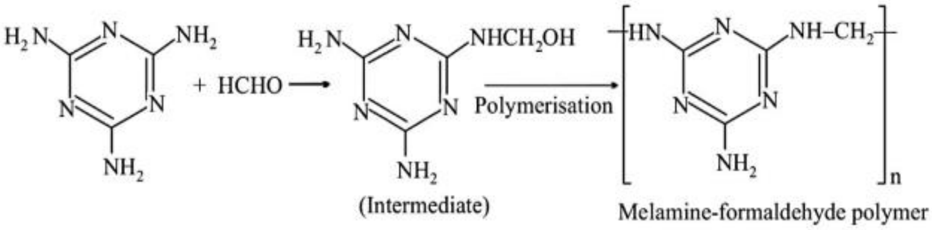
By far the largest use of synthetic polymers is as plastics and they do not get disintegrate by themselves. This non-biodegradability is due to the carbon-carbon bonds of addition polymers, which are inert to enzyme catalysed reaction. Hence Biodegradable polymers are taken into consideration. They are the polymers that can be broken into small segments by enzyme catalysed reaction using enzymes produced by micro-organisms.

Bonds that can be broken by the enzymes are inserted into the polymers. Therefore, they can be degraded by enzymes present in the ground.

Aliphatic polyesters are important class of biodegradable polymers. For example- PHBV (poly hydroxybutyrate-CO-β-hydroxy-valerate), poly glycolic acid, poly lactic acid etc.

8.9 MELAMINE-FORMALDEHYDE RESIN

This resin is formed by condensation polymerisation of melamine and formaldehyde.



Properties:

- Melamine is known for its excellent heat resistance. It can withstand high temperatures without decomposing.
- Melamine is resistant to many chemicals, including acids and bases.
- Melamine is a hard and durable material, making it resistant to wear and tear.
- Melamine is non-porous, which means it does not easily absorb liquids or bacteria, and it exhibits good electrical insulating properties as well.

Uses:

- Melamine is commonly used to manufacture plates, bowls, cups, utensils, and it is widely used in the production of decorative laminates for furniture and interior surfaces.
- Melamine is used as a coating material for wood and other surfaces to enhance their durability and resistance to moisture, chemicals, and abrasion.
- Melamine's electrical insulating properties make it suitable for use in the production of electrical components and insulating materials.
- Melamine is used in the textile industry as a cross-linking agent for resins, improving the durability and wrinkle resistance of fabrics.

Exercise - 1

1. What is monomer of Teflon? [CGPSC ACF 2017]
   (a) Tetrafluoroethene
   (b) Ethyle
   (c) Glycol
   (d) Propene
   (e) None of these

2. Which of the following is **not** a linear polymer? [CGPSC ACF 2017]
   (a) Polythene
   (b) Polyvinyl chloride
   (c) Polystyrene
   (d) Nylon – 66
   (e) None of these

3. A copolymer is formed when [CGPSC ACF 2017]
   (a) Two homopolymers react with each other
   (b) Two or more different monomers react with each other
   (c) Three identical homopolymers react with each other
   (d) Two identical monomers react with each other
   (e) None of these

4. Nylon threads are made up of [Raj ACF 2018]
   (a) Polyvinyl polymer
   (b) Polyamide polymer
   (c) Polyester polymer
   (d) Polyethylene polymer

5. Which one of the following is fully fluorinated polymer? [Raj ACF 2018]
   (a) Thiokol
   (b) Teflon
   (c) PVC
   (d) Neoprene

6. Neoprene is prepared by polymerisation of which of the following? [Raj ACF 2018]
   (a) 1, 3- butadiene
   (b) 2– chloro- 1, 3 butadiene
   (c) Acrylonitrile
   (d) 2-methyl – 1, 3- butadiene

7. Consider the following statements [CG pariyojna 2021]
   (A) Low density polythene consists of closely packed linear molecules.
   (B) Polyvinyl Chloride (PVC) is thermoplastic.
   (C) The tensile strength of high-density polythene is more than low density polythene.
   (D) Teflon is a heat resistant polymer.
   (E) Poly mono chloro-trifluoro ethylene (PCTFE) is a thermosetting polymer.

   Correct statements are:
   (a) 1, 2 and 3
   (b) 2, 3 and 4
   (c) 1, 2 and 5
   (d) 3, 4 and 5

8. Consider the following statements: [CG Pariyojna 2021]
   (A) The melting point of high-density polythene is high.
   (B) Teflon is a homopolymer.
   (C) Polyvinyl chloride is good conductor of heat and electricity.
   (D) Starch and cellulose are natural polymers.
   (E) Biodegradable polymers are ecofriendly.

   Wrong statements are:

   (a) A and B
   (b) B and C
   (c) A and C
   (d) D and E

9. Which was mismatched? [CG Vyapam RFO 2021]
   (A) Caprolactam – Backmann's rearrangement
   (B) Synthetic polymer – PDI (poly Dispersity Index) < 1
   (C) Teflon – Homopolymer
   (D) PVC – Eye lenses
   (E) Plasticiser for PVC – Esters of phthalic acid

   Codes:
   (a) A and B
   (b) B and D
   (c) C and D
   (d) A and E

10. Polymer obtained by the following process is: [CGPSC ACF 2020]

$$nCF_2 = CF_2 \xrightarrow[high\ pressure]{(NH_4)_2S_2O_8} ?$$

   (a) Nylon
   (b) Polypropylene
   (c) Oralon
   (d) None of these

11. Rayon is different from synthetic fibres because: [MHPSC forest Main 2022]

- (a) It is the other name of silk
- (b) It is obtained from wood pulp by chemical treatment.
- (c) It is a natural fibre and use as it is.
- (d) None of the above

12. Which of the following is monomer of P.V.C [MPPSC SFM 2018]
    - (a) Ethylene
    - (b) Vinyl chloride
    - (c) Acrylonitrile
    - (d) Ethylene glycol
13. Teflon is formed by polymerisation of the following monomer: [MPPSC SFM 2018]
    - (a) $CH_2 = CH_2$
    - (b) $CH_2 = CHCl$
    - (c) $CF_2 = CF_2$
    - (d) $C_6H_5CH = CH_2$
14. Which of the following is **not** a synthetic polymer? [MPPSC SFM SP 2019]
    - (a) Polythene
    - (b) Nylon -6, 6
    - (c) Buna-S
    - (d) Resins
15. Which of the following Is **not** an example of natural polymer? [MPPSC SFS Main 2019]
    - (a) Wool
    - (b) Silk
    - (c) Polyisoprene
    - (d) Nylon
16. In vulcanization, rubber is heated with following elements [MPPSC SFS Main 2019]
    - (a) Phosphorus
    - (b) Iodine
    - (c) Sodium
    - (d) Sulphur
17. $F_2C = CF_2$ is a monomer of following [MPPSC SFS Main 2019]
    - (a) Teflon
    - (b) Glyptal
    - (c) Nylon – 6
    - (d) Buna – S
18. Which one among the following is a thermosetting polymer? [MPPSC SFS Main 2019]
    - (a) PVC
    - (b) Nylon
    - (c) Bakelite
    - (d) Polystyrene
19. Match the following: [MPPSC SFS Main 2021]

(A) Neoprene	1. Ethyleneglycol and phthalic acid
(B) Buna -N	2. Phenol and formaldehyde
(C) Glyptal	3. Chloroprene
(D) Bakelite	4. 1, 3 – Butadiene and acrylonitrile

Codes

	(A)	(B)	(C)	(D)
(a)	3	4	1	2
(b)	3	4	2	1
(c)	4	3	2	1
(d)	4	2	3	1

Answer Key

1. a	2. e	3. b	4. b	5. b	6. b	7. b	8. c	9. b	10. d	11. b	12. b
13. c	14. d	15. d	16. d	17. a	18. c	19. a					

8.10 SOAP AND DETERGENTS

Soaps and detergents are both cleansing agents used for removing dirt, oil, and other contaminants from surfaces. They remove dirt by removing fats (which are responsible for binding other substances to skin or fabric). They also play an important role in enhancing the cleansing properties of water and are made up of a variety of different components. They both fall into the category of surfactants. Surfactants are compounds that lower the surface tension between two liquids or between a liquid and a solid. This property allows them to emulsify or disperse oils and grease in water.

- **Soap:** Soaps are potassium or sodium salts of a carboxylic acid having a long aliphatic chain attached to it [RCOONa]. Soap is traditionally made from fats and oils, which are triglycerides. Ex. Sodium palmitate and sodium stearate.
  1) **Making:** The most common method of making soap is through saponification, a chemical reaction that involves the hydrolysis of fats (glyceryl esters of fatty acids) with an alkali (such as sodium hydroxide for solid soap or potassium hydroxide for liquid soap). The resulting product of saponification is glycerol (glycerine) and soap molecules. The carboxylate end (Head) of the soap molecule is hydrophilic (water-attracting), whereas the hydrocarbon end (Tail) is hydrophobic (water-repelling). **Note:** sodium chloride is added to precipitate soap, and only sodium and potassium soaps are soluble in water.
  2) **Action:** Soap molecules surround oil droplets (hydrophobic substances) and form structures called 'micelles.' The hydrophobic tails of the soap molecules embed into the oil, while the hydrophilic heads face outward, allowing the oil to be dispersed in water.
  3) **Properties:**
     - Soaps are generally hard in nature, they are solid.
     - Soaps lather up when they come in-contact with soft water.
     - They are not effective in hard water and saline water.
     - They consist of a '-COONa' group attached to a fatty acid having a long alkyl chain.
     - They are derived from natural sources such as vegetable oils and animal fats.
     - Soaps are completely biodegradable hence environment friendly.
     - They form scum while reacting with hard water.
  4) **Uses:**
     - Soaps are generally utilized as surfactants in washing, bathing, and cleaning, but they are also used in lubricants and textile spinning.
- **Detergents:** Detergents are the potassium or sodium salts of a long alkyl chain ending with a sulfonate group or mono carboxylic acid. Ex. Sodium lauryl sulphate and deoxycholic acid.
  1) **Composition:** Detergents are synthetic surfactants and are often made from petrochemicals. They can be formulated to be more effective in hard water compared to soaps. The most common types of detergents are anionic (negatively charged), cationic (positively charged), non-ionic (no charge), and amphoteric (both positive and negative charges).
  2) **Action:** Detergents work similarly to soaps by lowering the surface tension of water and emulsifying oils and greases. They are generally more effective in hard water.

3) Properties:

- Detergents do not lose their effectiveness in hard water and saline water.
- They consist of a '-SO_3Na' group attached to a long alkyl chain.
- Detergents containing a branched hydrocarbon chains are non-biodegradable and thus they pollute more water than soaps.
- They do not form scum and are synthetic derivatives.
- These compounds can form a thick foam that causes the death of aquatic life.
- Laundry detergents generate micelles that include an organic chain of lipids and oils, and an ionic section that contains dirt and dust.

4) Uses:

- Detergents are widely used in cleaning products such as laundry detergents, dishwashing detergents, and multi-purpose cleaners.
- They are often chosen over soaps for laundry purposes, especially in areas with hard water, as they do not form insoluble precipitates with the minerals present in hard water.

Note:

- Anionic detergents are sodium salts of sulphonated long chain alcohols or hydrocarbons. They have anions at the soluble ends of the chains. The anionic portion of the molecule is involved in the cleansing effect of these detergents. They are generally used in the home (like soaps and toothpaste) to remove dirt, clay, and some oily stains. For example- sodium lauryl sulphate and sodium n-dodecyl benzene sulphonate.
- Cationic detergents are quaternary ammonium salts of amines with anions as acetates, chlorides, or bromides. The cationic part consists of a long hydrocarbon chain and a positively charge nitrogen atom. The centre ammonium sulphate is positively charged. They are used as wetting agents, fabric softeners, bacteriostats, and emulsifiers. For example- Cetyl-trimethyl-ammonium bromide, benzalkonium chloride etc.
- Non-ionic detergents do not contain any ions, and have a neutral group in their molecule. They are monoesters of high molecular mass alcohols and are very effective for dishwashing and other situations where inorganic ions are not allowed. For example- sodium alkyl sulphates, sodium alkyl benzene sulphonates etc.
- The polar head groups of Zwitterionic detergents contain both negatively and positively charged atomic groups, therefore the overall charge is neutral. The strength of action of these compounds considered to be intermediate between ionic and non-ionic detergents, sharing characteristics with both types. They are used in chromatography, different electrophoresis (2D gel electrophoresis), mass spectrometry etc. For example- CHAPS, SB-12, ASB-14 etc.

Exercise no 2

1. Sodium and potassium salt of long chain monocarboxylic acids are called [CGPSC ACF 2017]
   - (a) Soap
   - (b) Oil and fat
   - (c) Protein
   - (d) Detergent
   - (e) None of these
2. Lauryl alcohol ethoxylate is a [CG Vyapam RFO 2021]
   - (a) Anionic detergent
   - (b) Cationic detergent
   - (c) Non – iconic detergent
   - (d) Zwitter-ionic detergent
3. Soaps are sodium salts of following long chain compound [MPPSC SFS Main 2019]
   - (a) Fatty acid
   - (b) Alkyl sulphates
   - (c) Benzene sulphuric acid
   - (d) Amino acids
4. Sodium lauryl sulphate… [MPPSC SFS Main 2021]
   - (a) Is cationic detergent
   - (b) Is anionic detergent
   - (c) Is non - anionic detergent
   - (d) None of the above

(1.) d, (2.) a, (3.) a, (4) b

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